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CATALYTIC DESULFURIZATION AND DENITROGENATION

Charles N. Satterfield, et al

Massachusetts Institute of Technology

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16. ABSTRACT: The report gives results of a study of catalytic desulfurization and denitrogenation, using thiophene and pyridine as model compounds because they represent some of the less reactive organosulfur and organonitrogen compounds. When thiophene is hydrodesulfurized simultaneously with the hydrodenitrogenation of pyridine (200 to 500 C, 4.4 and 11.2 bars pressure, commercial catalysts), the two reactions are mutually inhibitive at lower temperatures. At high temperatures, H2S (a hydrodesulfurization reaction product) enhances the hydrodenitrogenation rate. The report proposes mechanisms to explain these observations. In hydrodenitrogenation of pyridine and other heterocyclic nitrogen compounds, the rate may be at least partly governed by the equilibrium of the first step, the hydrogenation of the N-containing ring.

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1. SUMMARY

The hydroprocessing of fuels containing relatively large amounts of organonitrogen compounds will become increasingly important in the future in the upgrading of synthetic fuels from oil shale and coal or processing of lower grades of crude petroleum. Organosulfur compounds are always also present and the inhibiting effect of organonitrogen compounds on catalytic hydrodesulfurization is established. However very little has been published on the effect of organosulfur compounds on hydrodenitrogenation. These two groups of effects were explored using as model compounds thiophene and pyridine which represent some of the less reactive organosulfur and organonitrogen compounds respectively.

Studies were made with a flow microreactor at temperatures of 200 to 500°C., 4.4 and 11.2 bars pressure, on commercial catalysts consisting of $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, NiW/Al_2O_3 and NiW/SiO_2-Al_2O_3. Pyridine hydrodenitrogenation (HDN) is more difficult than thiophene hydrodesulfurization (HDS). We find that pyridine inhibits the HDS reaction as previously reported, but sulfur compounds have a dual effect on HDN. At low temperatures, thiophene inhibits the reaction by competing with pyridine for hydrogenation sites on the catalyst. This retards the hydrogenation of pyridine to piperidine, reducing the overall reaction rate. At high temperatures the dominant effect is interaction of hydrogen sulfide, an HDS reaction product, with the catalyst to improve its hydrogenolysis (hydrocracking) activity. This increases the rate of piperidine hydrogenolysis, which is rate-determining at the latter conditions, and enhances the overall rate of HDN.

From studies of HDN of pyridine and piperidine in the absence of sulfur compounds we have established that equilibration between pyridine and piperidine, the first product formed in the overall series of hydrodenitrogenation (HDN) reactions of pyridine, can be a rate-limiting

factor under some conditions. Thus on a commercial $NiMo/Al_2O_3$ catalyst at 11 bars pressure a maximum in the pyridine HDN rate occurs at about 400°C, caused by a thermodynamic limitation on the allowable concentration of piperidine. $NiMo/Al_2O_3$ appears to have greater hydrogenation-dehydrogenation activity than $CoMo/Al_2O_3$ but $CoMo/Al_2O_3$ appears to have greater hydrogenolysis activity than $NiMo/Al_2O_3$, at least at about 300°C and below.

Thermodynamic analysis of the principal steps in the reaction of other representative heterocyclic nitrogen compounds (pyrrole, quinoline, isoquinoline, indole, acridine, and carbazole) reveals that under some significant reaction conditions the overall HDN rate of these compounds may likewise be at least partly governed by the equilibrium of the first step, the hydrogenation of the N-containing ring. There is no significant thermodynamic limitation on the principal subsequent steps or on the reaction as a whole.

2. INTRODUCTION

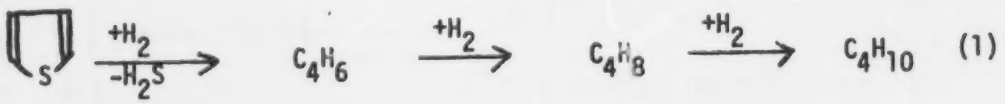
Hydrodesulfurization (HDS), which is accompanied by some hydrodenitrogenation (HDN), is an important commercial process for removal of organosulfur compounds from petroleum feedstocks. The overall chemical reactions involved are:

$$\left\{\begin{array}{l}\text{Organo-sulfur compound}\\ \\ \text{Organo-nitrogen compound}\end{array}\right\} + H_2 \xrightarrow[\text{catalyst}]{} \text{Hydrocarbon} + \left\{\begin{array}{l}H_2S\\ \\ NH_3\end{array}\right\}$$

Sulfided cobalt-molybdenum on alumina or nickel-molybdenum on alumina are typical catalysts. Several excellent reviews of HDS reactions and processes are available (Schuman and Shalit, 1970; Schuit and Gates, 1973; Weisser and Landa, 1973a).

Hydrodenitrogenation will become increasingly important in the future to lower the organonitrogen content of synthetic crudes extracted from oil shale, some coals or certain low-grade naturally-occurring petroleum, which contains large amounts of both sulfur and nitrogen. HDS and HDN occur simultaneously at suitable temperatures and pressures, but the reactions interact with each other in ways which are little understood. As will be shown, under some circumstances mutual inhibition occurs, under others, H_2S enhances HDN. This work was undertaken to elucidate these interactions by study of the HDS/HDN reactions of mixtures of thiophene and pyridine on four commercial hydrotreating catalysts. Some studies of HDN of pyridine and pyrrole were also made. These compounds were chosen because they are representative of classes of sulfur and nitrogen compounds in petroleum and synthetic fuels which are difficult to desulfurize and denitrogenate by hydrogenation.

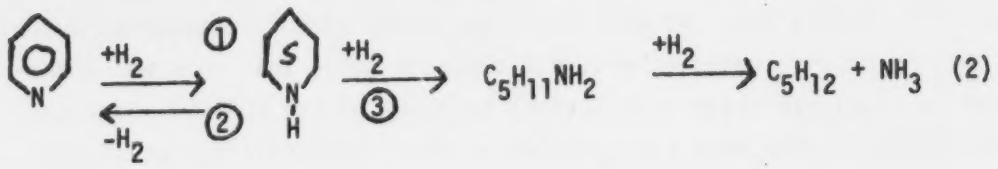
Studies on HDS of thiophene and HDN of pyridine have revealed substantial information about the reaction mechanisms for these compounds individually, although it is not too clear how these may be affected by pressure or by the nature of the catalyst. From studies at 1 atmosphere over chromia and supported cobalt molybdate catalysts, Owens and Amberg, (1961) proposed the following for the desulfurization of thiophene:



(1)

Their results specifically indicated that the first step, at least under their conditions, is cleavage of a C-S bond rather than hydrogenation of thiophene. The reaction rate has been described by a Langmuir-Hinshelwood expression in which thiophene and hydrogen sulfide compete for catalyst sites (Satterfield and Roberts, 1968). Hydrogen sulfide also inhibits the subsequent hydrogenation steps.

Pyridine is less reactive than thiophene. From studies on a supported nickel cobalt molybdenum catalyst at 750 to 1500 psig, McIlvried (1971) concluded that the mechanism of pyridine denitrogenation is



(2)

Disproportionation reactions of piperidine and pentyl amine also occur (Sonnemans et al., 1972). The rate of pyridine denitrogenation can also be described by a Langmuir-Hinshelwood model in which adsorbed nitrogen compounds have a strong inhibiting effect on the rate.

Pyrrole has seldom been used in HDN studies since its instability makes handling difficult.

Previous studies on simultaneous HDS/HDN indicate that nitrogen compounds inhibit the HDS process. In tests of 35 different crude oil fractions, Kiovsky and Berg (1964) concluded that the nitrogen content of the feedstock was the most important variable affecting catalyst HDS activity. Doelman (1962) studied the HDS of a cycle oil fraction (3.8 wt. % sulfur) to which he added pyridine and quinoline. With the processing conditions used, sulfur removal from the original cycle oil was 98%, while in the presence of the nitrogen compounds (1.0 wt. % nitrogen in feedstock) sulfur removal was 94%. Kirsch et al., (1959) experimented with a synthetic gasoline (0.4 wt % sulfur) blended from heptane, heptene, and thiophene. With their experimental conditions sulfur removal from this feedstock was 79%, while addition of pyridine (0.1 wt. % nitrogen in feed) reduced this to 59%. Ahuja et al. (1970) also observed pyridine inhibition of thiophene HDS over catalysts other than cobalt-molybdenum-alumina.

Two studies using pure compounds have also shown the detrimental effect of nitrogen compounds on HDS. Desikan and Amberg (1964) observed that pyridine poisoned thiophene HDS on a presulfided $CoMo/Al_2O_3$ catalyst in a manner indicating that there were two sites which have HDS activity. Pyridine apparently poisons these sites to different extents. Lipsch and Schuit (1969) also reported that pyridine poisons thiophene HDS, using a $CoMo/Al_2O_3$ catalyst that was prereduced but not presulfided, but the effect was not great as that of Desikan and Amberg. Both these studies utilized pulsed reactors, so the results are mainly qualitative.

The effects of sulfur compounds on HDN are only poorly understood. A patent by Gerald (1957) claimed the addition of a sulfur compound in great excess over the organo nitrogen present to improve nitrogen removal over a catalyst containing molybdenum, attributed to the possible formation or maintenance of a particular sulfided form of the catalyst. A recent study by Goudriaan et al. (1973) reported that hydrodenitrogenation of pyridine over a $CoMo/Al_2O_3$ catalyst was enhanced if the catalyst were presulfided rather than being reduced in hydrogen. In the presence of hydrogen sulfide in molar excess over the pyridine, the nitrogen removal was further increased, attributed to an enhancement of the hydrocracking activity of the catalyst by the hydrogen sulfide.

3. APPARATUS AND PROCEDURE

The apparatus (Figure 1) centered around a steady-state flow micro-reactor. An infusion pump (Harvard Apparatus Company) fed a liquid feed (thiophene, pyridine, or a mixture of these compounds) to the system through a length of heated capillary which served as a vaporizer. Pre-purified grade hydrogen was passed through a DEOXO purifier and molecular sieve (type 4A) drying column to remove traces of oxygen and water. The hydrogen and vaporized reactants were then mixed and flowed through several feet of preheater tubing before entering the reactor.

The reactor was a stainless steel tube (0.5 cm i.d., 11 cm long) bent into a U-shape and packed with catalyst. Catalyst particles were commercial extrudates crushed and sieved to 20/24 mesh. A typical catalyst charge was 1.5 grams, and a single charge was used throughout an entire series of experiments. Table I shows the catalysts used. Each was activated prior to the first experimental run by treatment with a mixture of hydrogen sulfide (10%) and hydrogen (90%) according to a temperature-time program specified by the manufacturer.

The reactor and pre-heater tubing were immersed in a fluidized sand bath which served as a constant temperature medium. Reactor temperature was monitored with a thermocouple mounted in the exit gas stream so that its tip was just above the end of the catalyst bed. Temperature was controlled to $\pm$ 1°C below 350°C and $\pm$ 2°C above 350°C.

Samples were taken from the reactor effluent stream with a gas sampling valve (Carle model 2014) and injected into a Varian 2820 gas chromatograph. The sampling valve was mounted in an oven heated to 150°C to prevent condensation of reactants or products. The columns used in the chromatograph were 20-foot Carbowax 20M on Chromosorb W. These highly polar column packings separated the reactants (thiophene, pyridine) very well, but the light reaction products (butanes, ammonia, hydrogen sulfide, etc.) were unresolved and appeared as a single peak. Since hydrogen was used as the carrier gas in the chromatograph, the

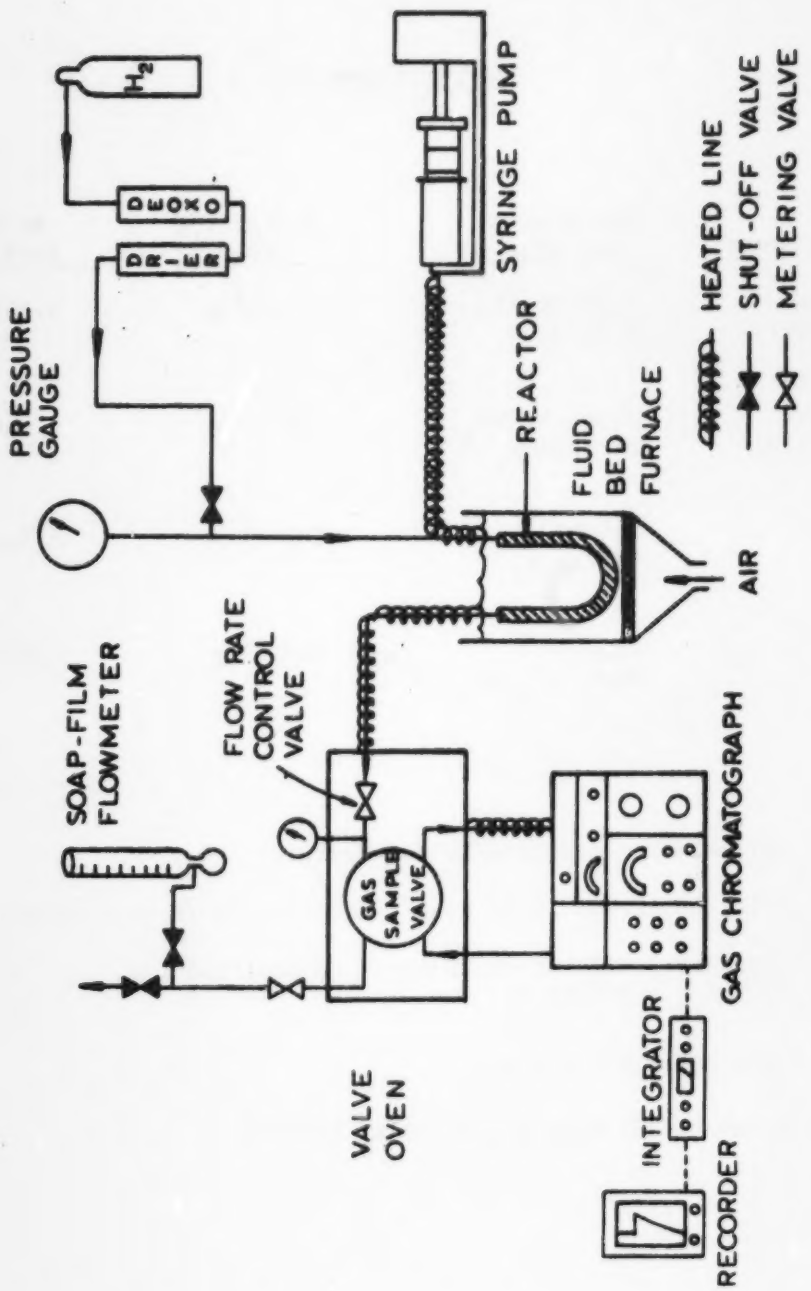


Figure 1. Schematic diagram of apparatus.

TABLE I

Catalysts Used

Manufacturer	Designation and Type	Surface Area (1)	Bulk Density (2)
American Cyanamid	Aero HDS-2A, $CoMo/Al_2O_3$	270 m^2/g	0.531 g/cc
American Cyanamid	Aero HDS-3A, $NiMo/Al_2O_3$ (a)	180 m^2/g	0.684 g/cc
Harshaw	Ni4303, NiW/Al_2O_3 (b)	152 m^2/g	0.765 g/cc
Harshaw	Ni4301 (3) $NiW/(SiO_2-Al_2O_3)$ (b)	228 m^2/g	0.847 g/cc

Notes:

(1) - Surface area reported by manufacturer

(2) - Bulk density of 20/24 mesh fraction used in experiments

(3) - Analysis indicated the support composition was: 66% SiO_2, 34% Al_2O_3

(a) 3.1 wt% NiO, 15.0 wt% MoO_3

(b) 6% Nickel and 19% tungsten, as metal content

hydrogen in samples of the reaction mixture did not appear on the chromatograms. Peak areas were determined with an electronic digital integrator.

A single experimental run consisted of determining the steady state fractional conversion of thiophene and of pyridine at each of several different reactor temperatures for a fixed quantity of catalyst, feedstock, pressure and total molar gas flow rate (hydrogen plus heterocyclic compounds) . In a series of experimental runs pressure, quantity of catalyst and gas flow rate were held constant but the ratio of thiophene and pyridine to each other and to hydrogen was varied from run to run. The feed rate of hydrogen was consequently adjusted slightly to keep the total molar flow rate constant as feed rates of thiophene and pyridine were changed. Hydrogen was always present in great excess, the mole ratio of hydrogen to heterocyclic compound varied from 22 to 90.

The raw data taken during a run were the reactant peak areas (thiophene, pyridine) and the overall flow rate through the system. Fractional conversions of the reactants were calculated for each reaction temperature of interest by taking the ratio of thiophene and pyridine peak areas to those found when no reaction was occurring.

The results showed very good reproducibility. The fractional conversions observed under a given set of conditions could be reproduced in separate experimental runs. With the analytical procedure used, however, a mass balance over the system was not possible. Application of correlations for heat transfer limitations (Mears, 1971) and mass transfer limitations (Satterfield, 1970) to worst-case conditions showed that no significant temperature or concentration gradients existed in the reactor. Further details on experimental procedures are given by Mayer (1974).

4. RESULTS: INTERACTIONS BETWEEN HDS OF THIOPHENE AND HDN OF PYRIDINE

4.1 HDS of Thiophene

Figures 2 and 3 show the percent conversion of thiophene obtained over a series of experimental runs using pure thiophene or mixed thiophene/pyridine feedstocks, each studied over a wide range of temperature. (See Table II for a summary of experimental conditions). The entire series of experiments was carried out with one catalyst charge. No reaction of the pyridine occurred in any of these runs. As shown in Figure 2, with pure thiophene feedstocks, the fractional conversion of thiophene increased as initial partial pressure was decreased, and further analysis showed that the rate was nearly zero order with respect to initial partial pressure over this range of conditions.

The presence of pyridine in the feedstock has a severe inhibiting effect on HDS, and changes the order of the HDS reaction, as is evident by comparison of the results with pure thiophene and those with mixtures of thiophene and pyridine. Comparison of runs 3/50 and 3/52 with 3/55 and 3/56 (Figure 2) shows that in the presence of pyridine the observed conversion of thiophene was independent of the initial concentration, indicating a rate expression which is first order with respect to initial thiophene partial pressure. Run 3/71, done as a reproducibility test (compare to 3/29, 3/35) after completion of the mixed feedstock experiments, showed an approximately 10% loss in HDS activity of the catalyst. This was the only permanent catalyst deactivation observed and it probably was caused by coke formation at the very high temperatures (500°C) reached in some of the mixed feedstock runs. Subsequent experiments were limited to 425°C. The inhibiting effect of pyridine was reversible.

Figure 3 shows the effect of varying the ratio of pyridine to thiophene, keeping the initial partial pressure of the two heterocyclic compounds constant at 142 torr. Small additions of pyridine have a major inhibiting effect but larger additions do not depress the rate further.

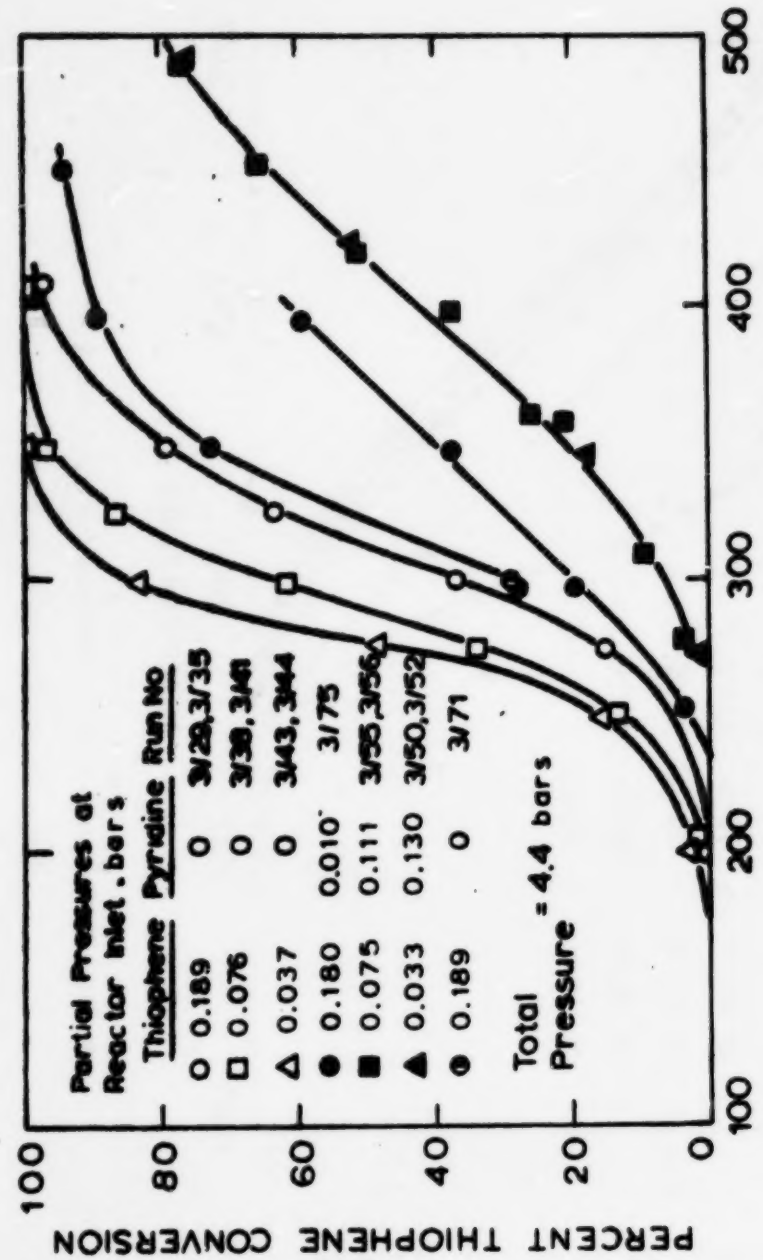

PERCENT THIOPHENE CONVERSION
TEMPERATURE, °C
Partial Pressures at Reactor Inlet, bars
Thiophene Pyridine Run No
○ 0.189 0 3/29,3/35
□ 0.076 0 3/38, 3/41
△ 0.037 0 3/43, 3/44
● 0.180 0.010 3/75
■ 0.075 0.111 3/53,3/56
▲ 0.033 0.130 3/50,3/52
● 0.189 0 3/71
Total Pressure = 4.4 bars

Figure 2. Thiophene HDS with CoMo/Al_2O_3 Catalyst.

(Experimental conditions given in Table II.)

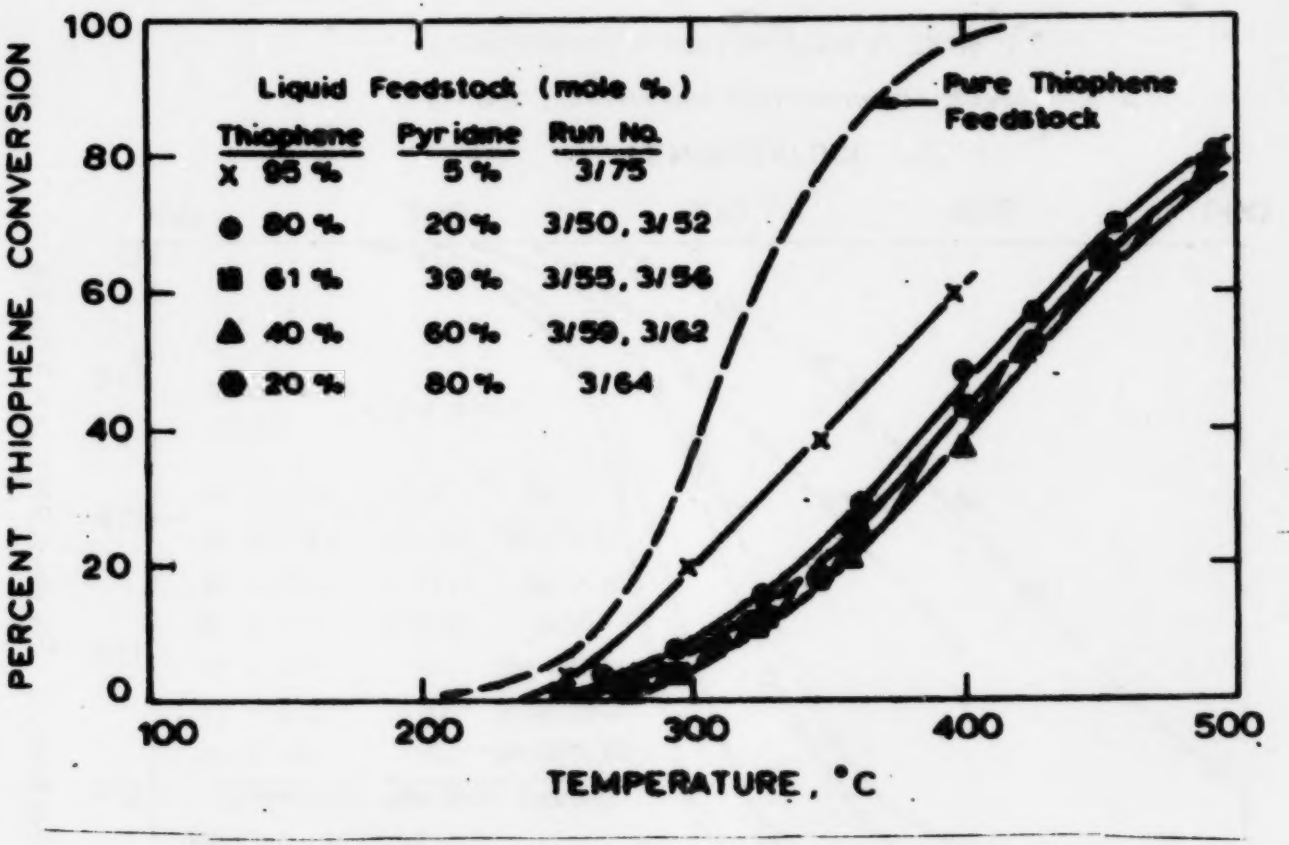


Figure 3. Thiophene HDS in mixed feedstocks with $CoMo/Al_2O_3$ Catalyst.

(Experimental conditions given in Table II.)

Table II

Experimental Conditions for Results Depicted in Figures

Figure #:	2,3	4,5	8	7	10
Pressure, bars:	4.4	11.2	4.4	11.2	11.2
Catalyst:	1.31 g (≈2.46cc) $CoMo/Al_2O_3$ 20/24 mesh	1.48 g (≈2.17cc) $NiMo/Al_2O_3$ 20/24 mesh	1.49 g (≈2.85cc) $CoMo/Al_2O_3$ 16/28 mesh	1.48 g NiW/SiO_2-Al_2O_3 20/24 mesh	1.48g $CoMo/Al_2O_3$ | NiW/Al_2O_3 20/24 mesh
Liquid Feed Rate, ml/hr	1.30 to 6.53	0.65 to 2.60	2.60	0.65 to 2.6	0.65 to 2.6
Hydrogen Feed Rate, av., cc(STP)/min	714	271	350	273	273
Residence Time,[1] sec.	0.52 to 0.32	3.1 to 2.1	≈1	2.44 to 1.65	3.77 to 2.55 | 2.65 to 1.80

1. Based on superficial linear velocity at reaction conditions (varies inversely with temperature).

Figure 4 shows the results of a similar series of runs, but at higher pressure (11.2 bars) and longer contact times, and using a $NiMo/Al_2O_3$ catalyst. HDN did occur in these runs, and those results will be discussed immediately below. As was observed at the lower pressure on the $CoMo/Al_2O_3$ catalyst, adding an equimolar amount of pyridine to a thiophene feedstock significantly reduces the fractional conversion of thiophene (compare 5/26 with 5/13, 5/16), while further increments of pyridine have very little additional effect (compare 5/34 and 5/36 with 5/26). As with the $CoMo/Al_2O_3$ catalyst, in the presence of large quantities of pyridine the HDS of thiophene follows nearly first order rate behavior, with conversion approximately independent of initial thiophene concentration (compare 5/29 and 5/31 with 5/26). Similar studies with NiW/Al_2O_3, NiW/SiO_2-Al_2O_3 and $CoMo/Al_2O_3$ catalysts at the same conditions (Mayer, 1974, pp. 86-87) showed virtually identical results to those obtained with $NiMo/Al_2O_3$. Although the same weight of each catalyst was used in this comparison the surface area per unit weight and the concentration of the active ingredients were somewhat different on different catalysts, so that a detailed comparison cannot be made quantitatively.

In summary the principal observations on the HDS reaction are (1) small additions of pyridine cause a major inhibition of the HDS of thiophene but larger additions have little effect, (2) thiophene HDS is zero order in the absence of pyridine and first order in the presence of substantial quantities, and (3) there is no significant difference between the behavior of the four catalysts studied.

4.2 HDN of Pyridine

Figure 5 presents the results for the HDN of pyridine alone on a $NiMo/Al_2O_3$ catalyst and in mixtures with thiophene as discussed above. Pyridine is much less reactive than thiophene. The maximum pyridine conversion ever observed was 50%, whereas thiophene could be 100% converted. The effect of temperature on HDN is unusual in that the fractional conversion goes through a maximum and turns downward above 380°C. This is probably because of the onset of a thermodynamic limitation on the reaction as discussed below. Comparison of runs 5/34 and

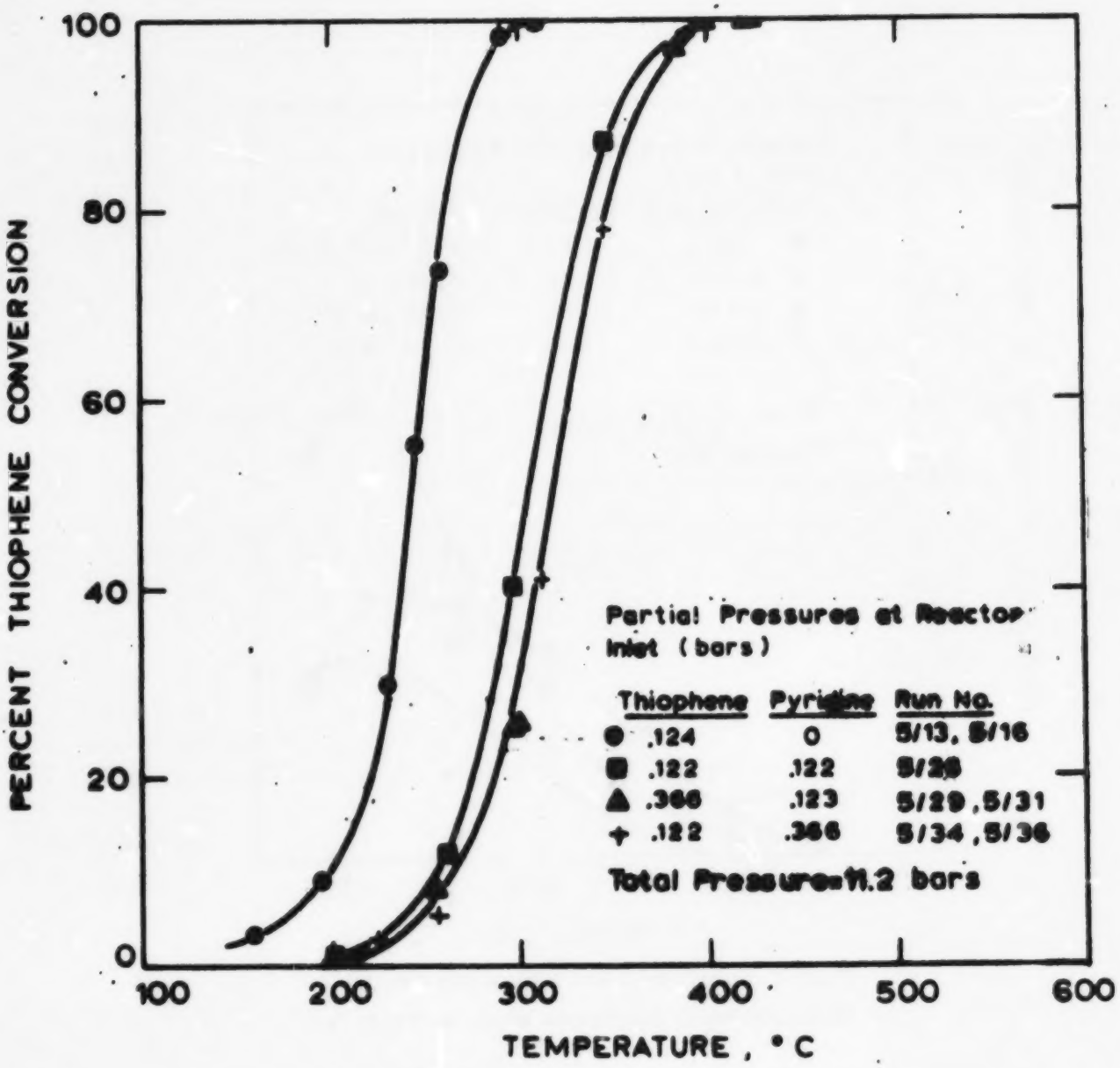


Figure 4. Thiophene HDS with $NiMo/Al_2O_3$ Catalyst.
(Experimental conditions given in Table II.)

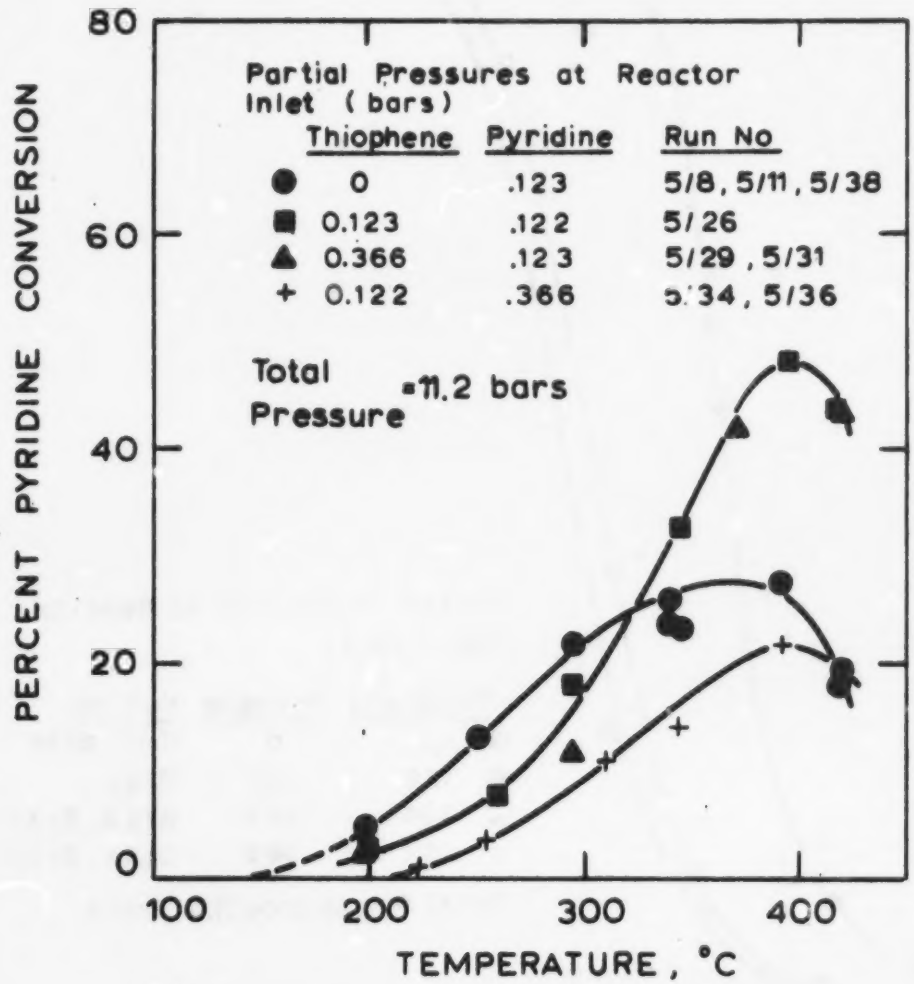


Figure 5. Pyridine HDN with $NiMo/Al_2O_3$ Catalyst.
(Experimental conditions given in Table II.)

5/36 with run 5/26 and other observations indicate that the HDN reaction here is between zero and first order over the entire temperature range.

The effect of thiophene on HDN is two-fold. Below 325°C the presence of the sulfur compound inhibits the HDN reaction, in that lower fractional pyridine conversions were observed with mixed feedstocks than with pure pyridine feedstocks. Above 325°C the presence of thiophene enhances the HDN reaction. However, thiophene itself is probably not responsible for the enhancement effect since it is more than 60% converted to hydrogen sulfide at 325°C (see Figure 4). To determine the role of hydrogen sulfide, three runs were performed with a pure pyridine feedstock at 10.3 bars total pressure but with a hydrogen sulfide partial pressure of 0.358 bar or 0.0046 bar in the reaction gas (Figure 6). With the higher H_2S partial pressure the results duplicated those of runs 5/29 and 5/31, thus confirming the hypothesis that hydrogen sulfide, not thiophene, is responsible for the enhancement effect on HDN. With 0.0046 bar H_2S, inhibition effects similar to those observed with thiophene appear but enhancement of HDN at the higher temperatures, although evident, is much reduced in magnitude from that observed in the other runs.

The effect of H_2S is corroborated by the observation of Goudriaan (1974 p. 157) on the hydrodenitrogenation of pyridine on a $CoMo/Al_2O_3$ catalyst at 75 bars pressure and 250-350°C. With a previously sulfided catalyst, a 2 to 6 fold increase in HDN activity was found in the presence of 4 bar pressure of H_2S over that found in the absence of H_2S.

Similar studies were made with the other three catalysts. As with the NiMo catalyst, in the presence of thiophene a maximum was observed with $CoMo/Al_2O_3$ or NiW/Al_2O_3 but somewhat different behavior occurred on NiW/SiO_2-Al_2O_3 (Figure 7). These effects will be discussed below.

The enhancement of HDN by H_2S may be associated with the maintenance of the catalyst in a completely sulfided state which has better HDN activity since the catalyst loses sulfur in the presence of hydrogen alone, as shown by some simple experiments. Correctly sulfided

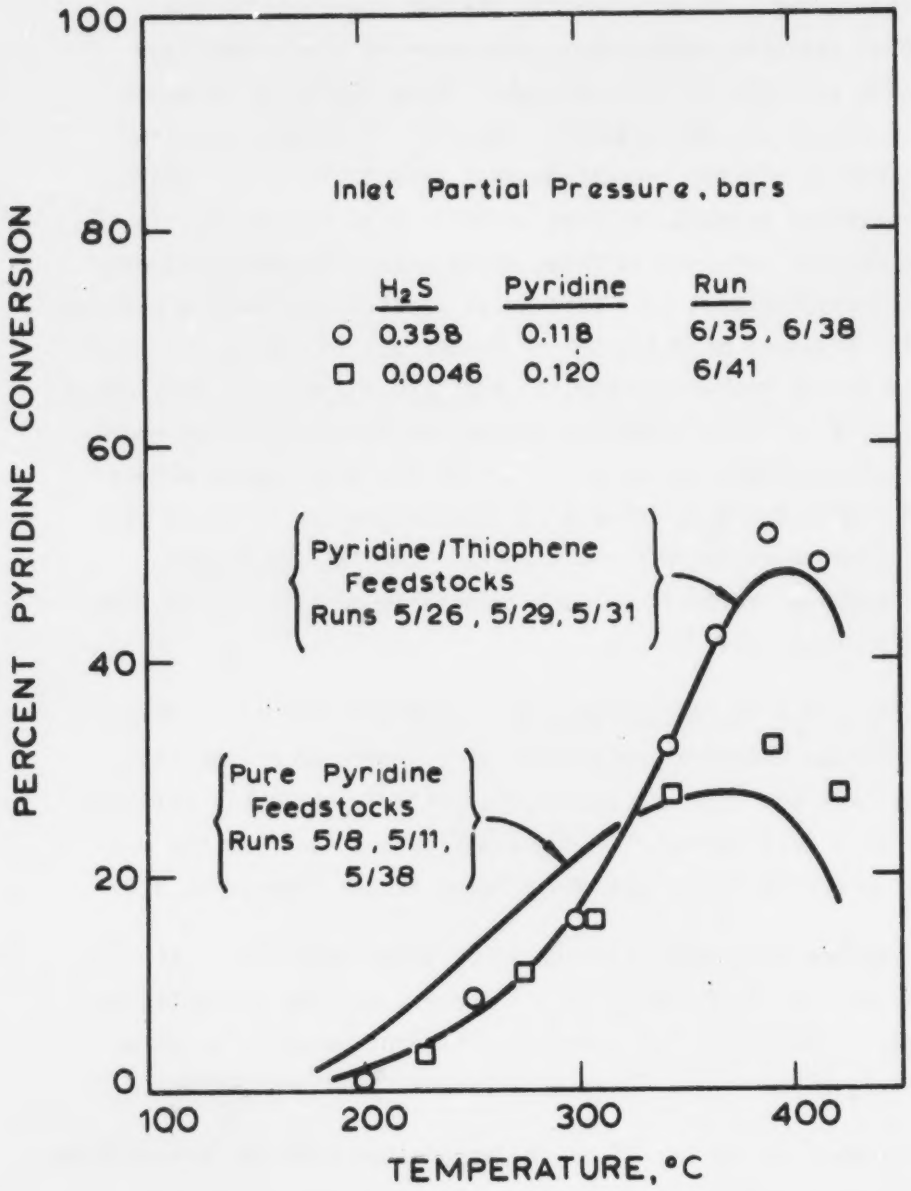


Figure 6. Pyridine HDN in presence of H_2S.

($NiMo/Al_2O_3$ Catalyst.)

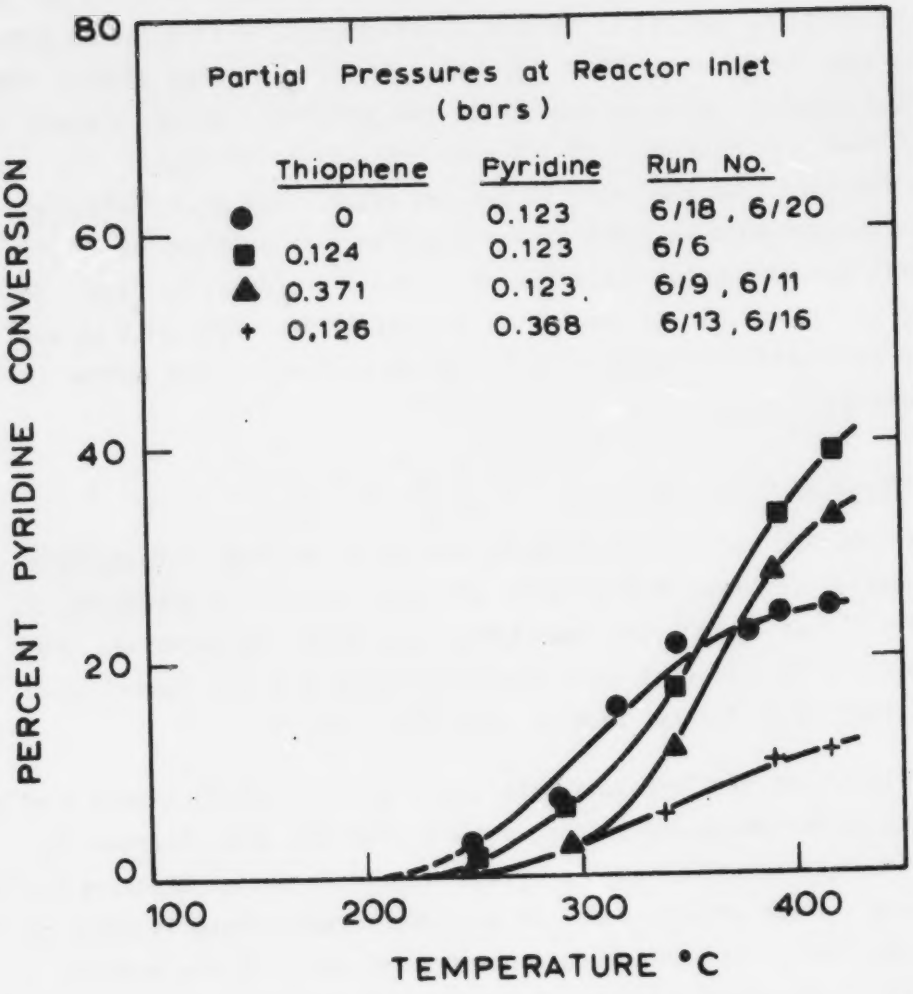


Figure 7. Pyridine HDN with NiW/(SiO_2 - Al_2O_3) Catalyst.

(Experimental conditions given in Table II.)

$CoMo/Al_2O_3$ had a sulfur content of 1.9 to 2.1 wt. % S, but after exposure to H_2 at either 300 or 400°C for 35 to 40 hours this was reduced to 1.0%.

Some scouting experiments (Mayer, p. 100, 1974) indicated that HDN activity will drop rapidly just after H_2S is removed from the reactant gas stream but further prolonged exposure to hydrogen will have little further effect beyond the initial decline. For example, at 350°C, on $CoMo/Al_2O_3$ catalyst, a 50/50 thiophene-pyridine feed gave a 31% conversion of pyridine and 93% conversion of thiophene. With pyridine alone at the same conditions, about 18% conversion was obtained after a freshly sulfided catalyst had been exposed to the pyridine-hydrogen mixture for only 1 hour, which dropped to 16% conversion after 38 hours. The rate of sulfur loss from the catalyst was not established quantitatively, but chromatographic analyses showed appearance of substantial H_2S in the exit gas during the first hour at a rapidly decreasing rate. The active sulfur-containing species on the catalyst surface must be unstable and rapidly decomposed in the absence of sufficient sulfur in the feed gas.

4.3 Effect of Other Additives

A few runs under limited conditions were performed with pyrrole, with results as shown in Figure 8. Although pyrrole is non-basic, it exhibits almost exactly the same inhibiting effect as pyridine. Work with pyrrole is difficult experimentally because of its thermal decomposition so no further studies were made with it.

Dilution of the feedstock with 1,3,5 triethylbenzene showed a mild increase in thiophene conversion, a trend that was also observed for pure thiophene feedstock as the initial reaction partial pressure was decreased. These results indicate that the reaction rate is close to zero order in initial thiophene concentration and that the aromatic compound is essentially inert under these sets of circumstances.

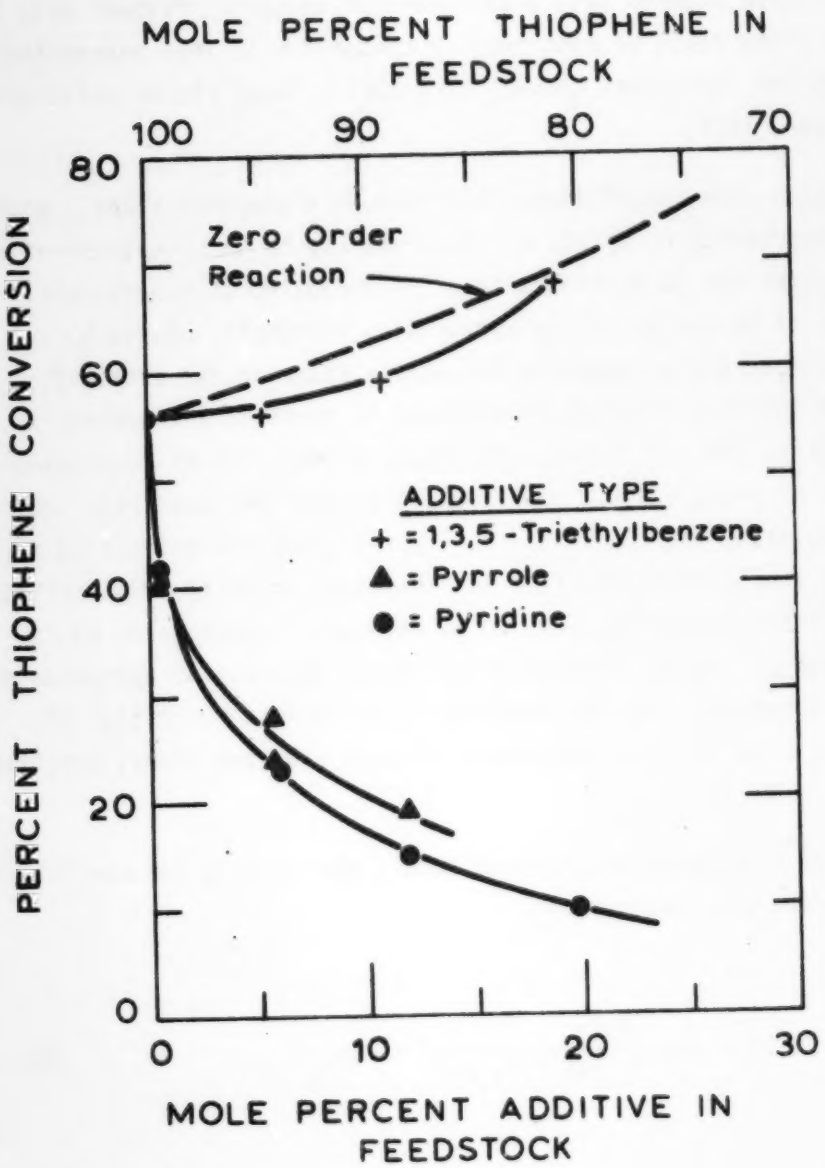


Figure 8. Effect of additives on Thiophene HDS at 300°C, 50 psig (other experimental conditions given in Table II.)

5. A MODEL FOR THE HDS OF THIOPHENE IN PRESENCE OF PYRIDINE

The HDS of thiophene is inhibited by H_2S and a kinetic expression for this reaction on $CoMo/Al_2O_3$ catalyst was developed by Satterfield and Roberts (1968) from studies with a differential reactor. Present data for thiophene HDS alone could be most readily compared with that expression for studies at low fractional conversion (<20%). These showed quite good agreement (Mayer, 1974).

Present data were insufficient to construct a complete kinetic model for HDS in the presence of pyridine. Nevertheless certain features of a satisfactory model can be developed from the following considerations. The inhibition of thiophene HDS by pyridine is presumably caused by competition between these compounds for active sites on the catalyst. The pattern of inhibition can be interpreted in terms of a two-site model analogous to that of Desikan and Amberg (1964). It is postulated that two kinds of sites (Type I and Type II) on sulfided catalysts are capable of catalyzing the HDS reaction. Type I sites are postulated to be very active and to be responsible for the majority of the HDS activity with pure thiophene feedstocks, but to be extremely sensitive to basic nitrogen compounds. In the absence of pyridine, the rate is approximately zero order in thiophene. In the presence of sufficient quantities of pyridine, these sites will be completely blocked and, therefore, inactive for HDS.

In terms of a Langmuir-Hinshelwood model, the results are consistent with the following rate expression:

$$r_I = \frac{k_I p_T}{1 + K_{I,T} p_T + K_{I,p} p_p} \times f(p_{h_2}) \qquad (3)$$

where $K_{I,T}p_T \gg 1$ and $K_{I,p}p_p \gg K_{I,T}p_T$ (For a more complete model a term for H_2S should be included in the denominator and the adsorptivity of H_2S relative to thiophene and pyridine should be considered.)

Type II sites are postulated to have less HDS activity, but to be less susceptible to poisoning, and therefore are responsible for the HDS activity of the catalyst after all Type I sites are blocked. Thiophene and pyridine probably compete for Type II sites, but the competition is less one-sided than on Type I sites.

Under moderate-to-high concentrations of pyridine, the rate of HDS is first order in thiophene and relatively insensitive to variations in pyridine concentration. These results are consistent with the following rate expression:

$$r_{II} = \frac{k_{II} p_T}{1 + K_{II,T} p_T + K_{II,P} p_P} \times f(p_{H_2}) \qquad (4)$$

where $K_{II,T} p_T \ll 1$ and $K_{II,P} p_P \ll 1$

The total rate of HDS is:

$$r = r_I + r_{II} \qquad (5)$$

In the absence of pyridine, the type I sites carry the reaction. That is $k_I \gg k_{II}$, or

$$r = \frac{k_I}{K_{I,T}} \times f(p_{H_2}) \qquad (6)$$

On the other hand, type II sites are much less sensitive to pyridine poisoning. Thus, in the presence of pyridine,

$$r = \frac{k_I p_T}{K_{I,P} p_P} \times f(p_{H_2}) + k_{II} p_T \times f(p_{H_2}) \qquad (7)$$

$$\simeq k_{II} p_T \times f(p_{H_2})$$

The inhibiting effects of pyridine on thiophene HDS found here follow the same trends observed by investigators studying the effects of nitrogen compounds on the HDS of real or simulated petroleum feedstocks. These

results indicate that sulfur removal by HDS from feedstocks having a high nitrogen content will be more difficult than sulfur removal from conventional, low-nitrogen feedstocks. This means more severe and consequently, more expensive processing conditions will be required, such as higher pressures, higher temperatures and longer contact times.

6. PYRIDINE HYDRODENITROGENATION: AN EQUILIBRIUM LIMITATION ON THE FORMATION OF PIPERIDINE INTERMEDIATE

6.1 Introduction

The mechanism of HDN of pyridine is given by Equation 2. Focussing on steps 1, 2 and 3, the equilibrium between pyridine and piperidine can affect the overall rate of reaction if step 3, hydrogenolysis of the C-N bond, is slower than step 1 and if conditions are such that the equilibrium concentration of piperidine is severely limited. The rate of hydrogenolysis of the C-N bond (and the overall HDN rate) is then less than it would be if there were no significant thermodynamic limitation on the concentration of piperidine. However, if step 1 were rate-limiting, piperidine would react as it forms and the position of the ring-saturation equilibrium would not influence the overall HDN rate.

Equilibrium towards piperidine becomes less favorable at higher temperatures and lower hydrogen pressures. Under the reaction conditions of McIlvried (315°C, 50-100 bars, NiCoMo/Al_2O_3 catalyst) hydrogenation was rapid and step 3 was rate-limiting. Equilibrium of steps 1 and 2 was far to the right. Stengler et al. (1964), as reported by Goudriaan (1974), stated that on a NiW/Al_2O_3 catalyst at 50 bar, step 3 was rate-limiting below 350°C and step 1 at higher temperatures. In a very recent study on CoMo/Al_2O_3 catalyst at 80 bars, Goudriaan (1974) concluded that the equilibrium of steps 1 and 2 may begin to limit the overall rate of reaction at temperatures higher than 350°C, and Sonnemans and co-workers (1973, 1974) discuss its implications for the mechanism of pyridine HDN. The study of simultaneous HDN and HDS (Sections 4, 5) found, unexpectedly, that the conversion of pyridine over some catalysts dropped with an increase in temperature above about 400°C. This effect apparently has not been previously reported in HDN studies and it can be interpreted in terms of the development of an unfavorable equilibrium for the initial saturation step at higher temperatures.

For this portion of the study, liquid pyridine or piperidine was pumped into the reactor system, vaporized, and mixed with hydrogen

before entering the reactor. A gas chromatograph equipped with Pennwalt 223 analytical columns was used for quantitative analysis of the reactor off-gas. Catalysts were commercial $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$ as used previously, crushed and sieved to provide a 20/24 mesh size for study. A single charge of each catalyst was used for all experiments. All studies were made at a total pressure of 11.2 bars and temperatures varied from about 200°C to 425°C. A great excess of H_2 was present at all times. The ranges of reactant partial pressure and space velocity (expressed here as a superficial residence time calculated for 250°C) are given in Table III. The analytical columns provided good separation of the heavier components (pyridine, piperidine, n-pentylamine), but the light reaction products such as ammonia and n-pentane, though they appeared as separate peaks on the chromatograms, were not resolved. Injection of known pyridine-piperidine solutions covering the full range of compositions indicated that the quantitative analysis of these components always involved absolute errors less than 0.5 mole per cent. Further details are given by Cocchetto (1974).

6.2 Results and Discussion

6.2.1 The Equilibrium Limitation: The percent conversions of pyridine as a function of temperature agreed closely with those we found in the previous studies for similar residence times. As before, greater conversions were obtained with $NiMo/Al_2O_3$ than with $CoMo/Al_2O_3$ over the entire temperature range investigated but even with $NiMo/Al_2O_3$ the conversion of pyridine reached a maximum of only 28% at about 375°C and then dropped (Figure 9). With piperidine HDN however, conversion increased with temperature on both catalysts, ultimately to the 100% level.

In order to focus on the reversible pyridine-piperidine reaction, Figure 10, Figure 11 (for $NiMo/Al_2O_3$) and Figure 12 (for $CoMo/Al_2O_3$) compare the experimentally observed ratios of piperidine to pyridine plus piperidine in the reactor effluent with the calculated equilibrium ratios (Cocchetto, 1974) as a function of temperature, for both pyridine HDN runs and piperidine HDN runs. The equilibrium curve corresponds to the hydrogen partial pressure of 11.1 bars. Figure 11 shows that for pyridine HDN, the amount

Table III

Experimental Conditions for HDN Studies

Total Pressure = 11.2 bars

Reaction of Pyridine

Catalyst	Partial Pressure at Reactor Inlet, bars	Superficial Residence Time (sec) at 250°C [a]
$NiMo/Al_2O_3$	0.13	3.04
$CoMo/Al_2O_3$	0.56	3.92
	0.55	7.91

Reaction of Piperidine

Catalyst	Partial Pressure at Reactor Inlet, bars	Superficial Residence Time (sec) at 250°C [a]
$NiMo/Al_2O_3$	0.12	3.08
$CoMo/Al_2O_3$	0.60	10.8

a. Residence time is calculated based on the superficial gas velocity at 250°C and 11.2 bars

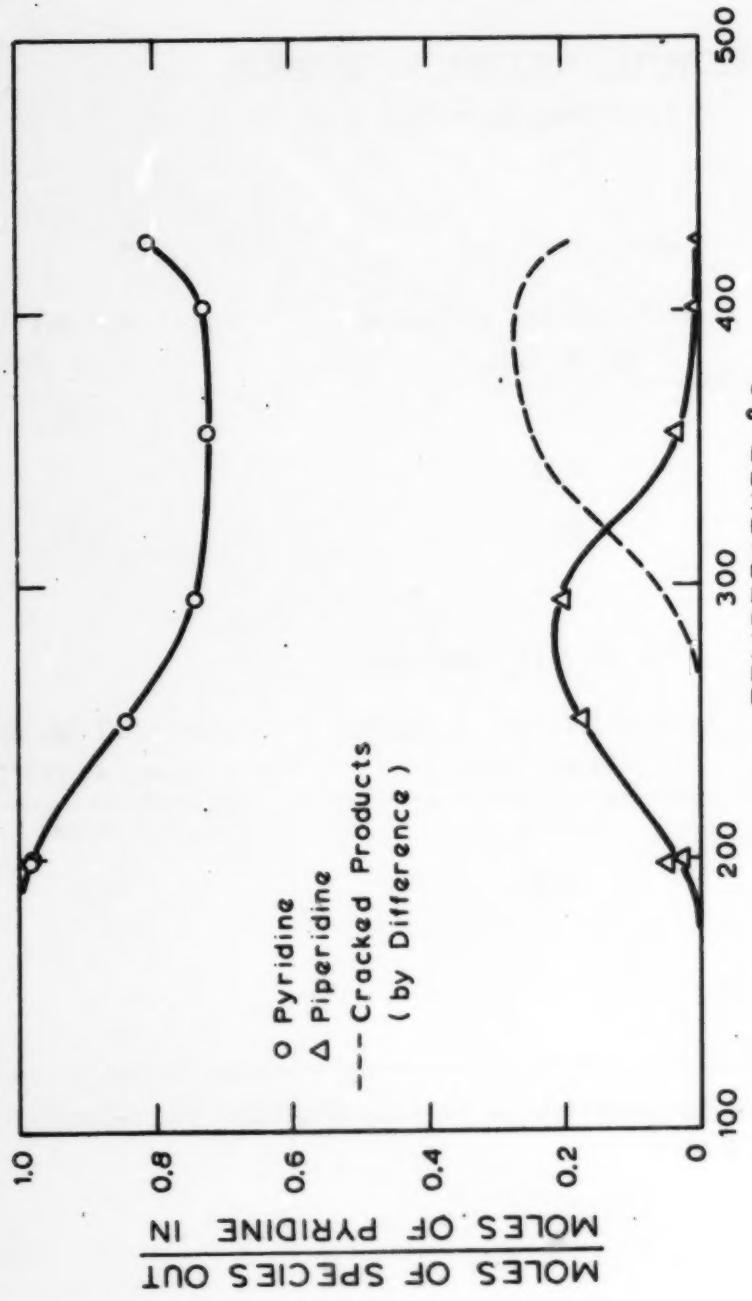


Figure 9. Product distribution for Pyridine HDN over NiMo/Al_2O_3 Catalyst.

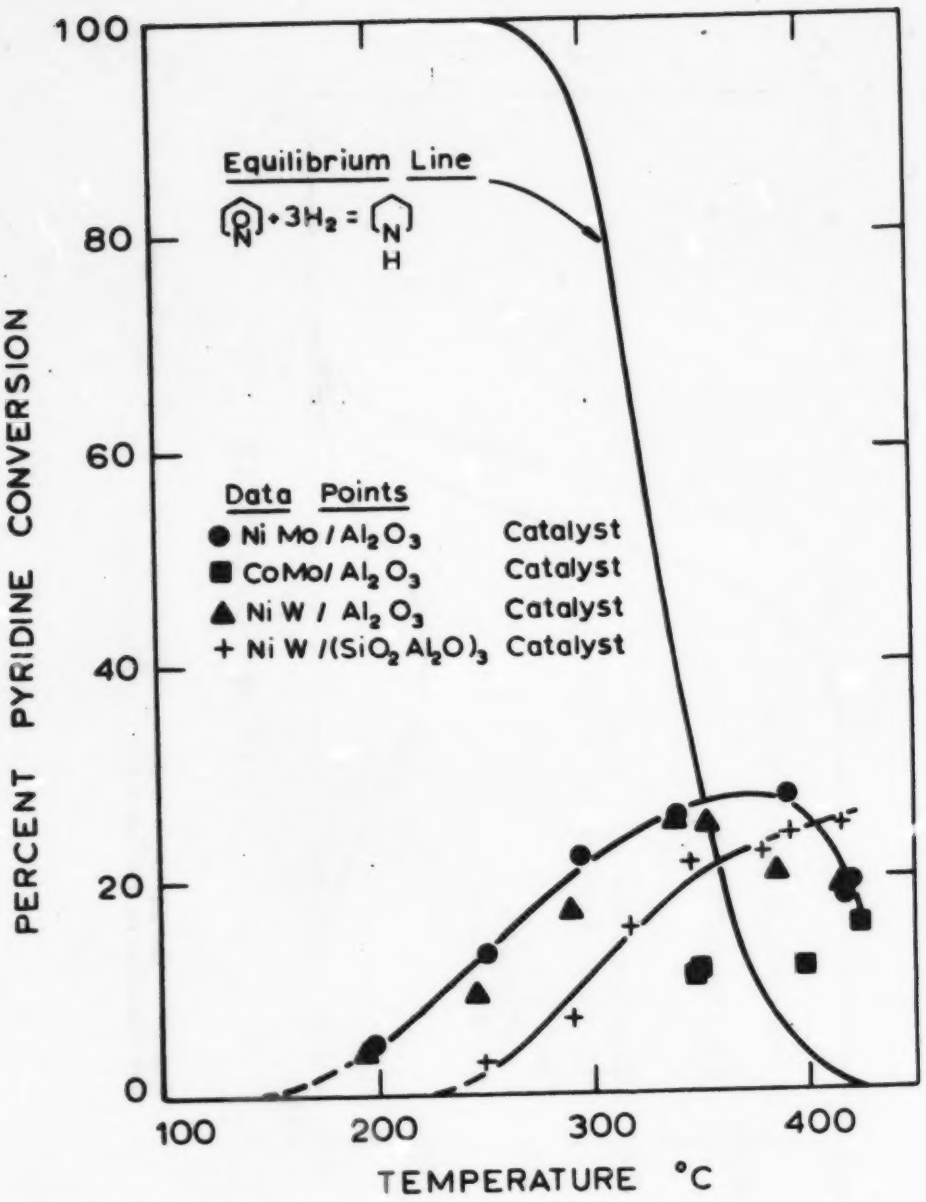


Figure 10. Comparison of experimental and Equilibrium Pyridine conversion. (Experimental conditions given in Table II.)

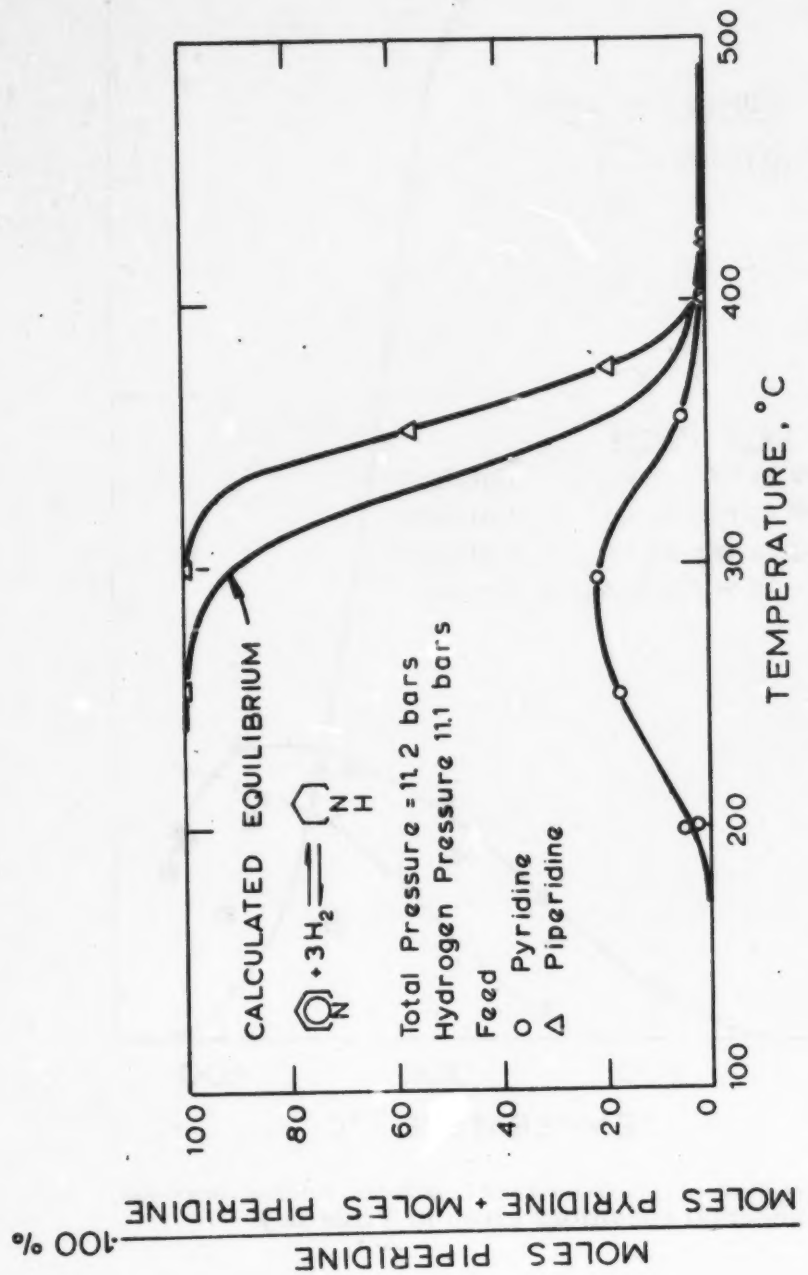


Figure 11. Comparison of experimental and Equilibrium quantities of Pyridine and Piperidine for HDN over NiMo/Al_2O_3 Catalyst.

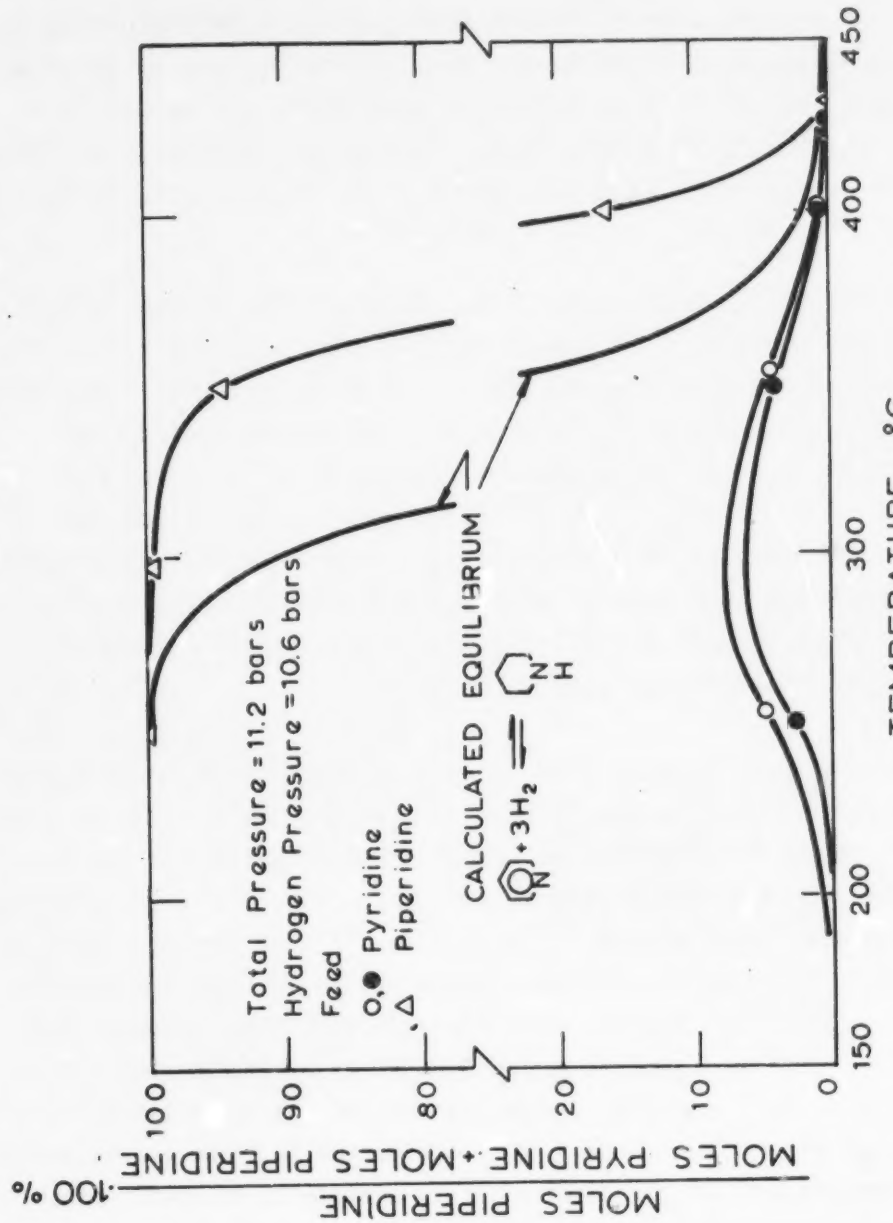


Figure 12. Comparison of experimental and Equilibrium quantities of Pyridine and Piperidine for HDN over $CoMo/Al_2O_3$ Catalyst.

of piperidine in the off-gas increased at the expense of pyridine as the temperature was increased to nearly 300°C. At this point, the equilibrium begins to shift from piperidine to pyridine, and the observed quantities of piperidine began to decrease with temperature. Above approximately 400°C, equilibrium was established. With piperidine feed, no pyridine was observed below 300°C but above this temperature its quantity increased steadily at the expense of the piperidine. At 400°C, equilibrium was again established. At high temperatures, equilibrium was established starting with either pyridine or piperidine.

The results shown in Figure 12 are quite similar, the two sets of data for pyridine feed representing two different residence times. The pyridine-piperidine reaction was generally farther from equilibrium with $CoMo/Al_2O_3$ than with $NiMo/Al_2O_3$, although the activities of the two catalysts cannot be precisely compared here since different partial pressures of reactant were used in the two cases. Equilibrium was finally established at 430°C with the piperidine feed, and at a slightly lower temperature (about 400°C) starting with pyridine. The results in the two figures clearly show the reversibility of pyridine saturation in the initial step of its hydrodenitrogenation.

6.2.2 Product Distribution: Some information about the relative hydrogenation and hydrogenolysis activities of the two catalysts can be gleaned from the product distributions as a function of temperature. For pyridine HDN Figure 9 shows results over $NiMo/Al_2O_3$ and Figure 13 over $CoMo/Al_2O_3$. No n-pentylamine was detected in the reactor effluent and the light reaction products (ammonia, n-pentane) could not be analyzed for quantitatively. The sum of ammonia, nitrogen-containing side products, and hydrocarbons such as n-pentane was determined by a material balance between the moles of pyridine fed to the reactor and the moles of pyridine and piperidine found in the products and is shown as the dashed lines. Ammonia was the principal nitrogen-containing cracked product, but at higher temperatures several light products other than ammonia and n-pentane appeared. With $NiMo/Al_2O_3$, below about 275°C piperidine was the only reaction product, and the material balance was within a

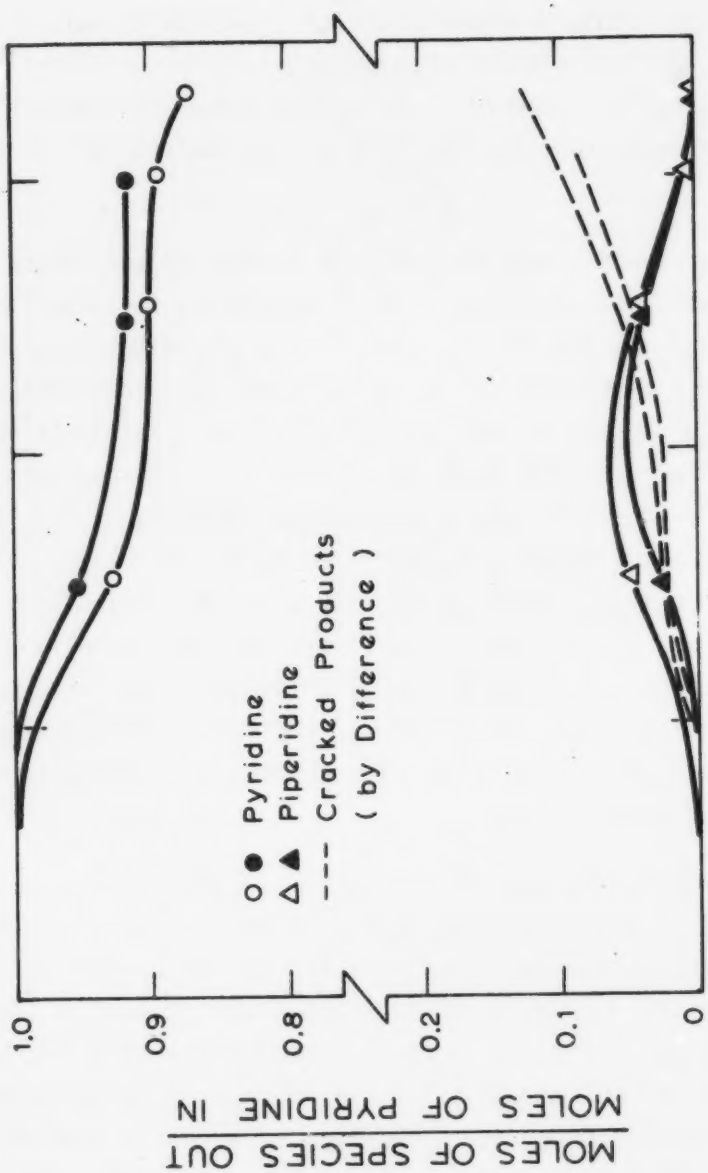


Figure 13. Product distribution for Pyridine HDN over CoMo/Al_2O_3 Catalyst.

few percent. The amount of piperidine in the reactor effluent reached a maximum just below 300°C and dropped to nearly zero at high temperatures. Ammonia and n-pentane were not observed at 251°C but were found in appreciable quantities at 295°C. Much greater quantities of ammonia and other light products appeared at 356°C and 402°C, but a decrease was observed at 426°C consistent with the downturn in pyridine conversion. With $CoMo/Al_2O_3$ less piperidine was always formed than with $NiMo/Al_2O_3$ at the same temperature and the ratio of cracked products to piperidine was higher.

Figures 14 and 15 are analogous to Figures 9 and 13 and show the product distribution as a function of temperature for piperidine HDN over $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$. With $NiMo/Al_2O_3$ up to about 40% of the piperidine was dehydrogenated to pyridine but the conversion of piperidine to cracked products (dashed line) reached a maximum at about 370°C and then decreased. This behavior is similar to the downturn in pyridine conversion observed for this same catalyst. With $CoMo/Al_2O_3$ (Figure 15) pyridine was again formed only above 300°C, but in smaller quantities than with $NiMo/Al_2O_3$. Small quantities of n-pentylamine were observed in the off-gas from 300-400°C. With both catalysts ammonia was the principal nitrogen-containing cracked product, and was produced in greater quantity than n-pentane. Qualitative examination of chromatogram peaks revealed trends consistent with the quantities of cracked products as calculated by difference.

Below 300°C only cracked products were formed with both $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, since the dehydrogenation of piperidine to pyridine was thermodynamically unfavorable. Comparison of the product distributions for pyridine and piperidine HDN over each catalyst suggest that below about 300°C, the hydrogenation of pyridine to piperidine was easier than piperidine hydrogenolysis for $NiMo/Al_2O_3$, but hydrogenolysis was easier than hydrogenation for $CoMo/Al_2O_3$. This could account for the low activity of $CoMo/Al_2O_3$ for pyridine HDN at low temperatures. The larger quantities of pyridine formed with $NiMo/Al_2O_3$ than with $CoMo/Al_2O_3$ for piperidine HDN also imply that the former catalyst had greater dehydrogenation activity. This is consistent with the fact that the piper-

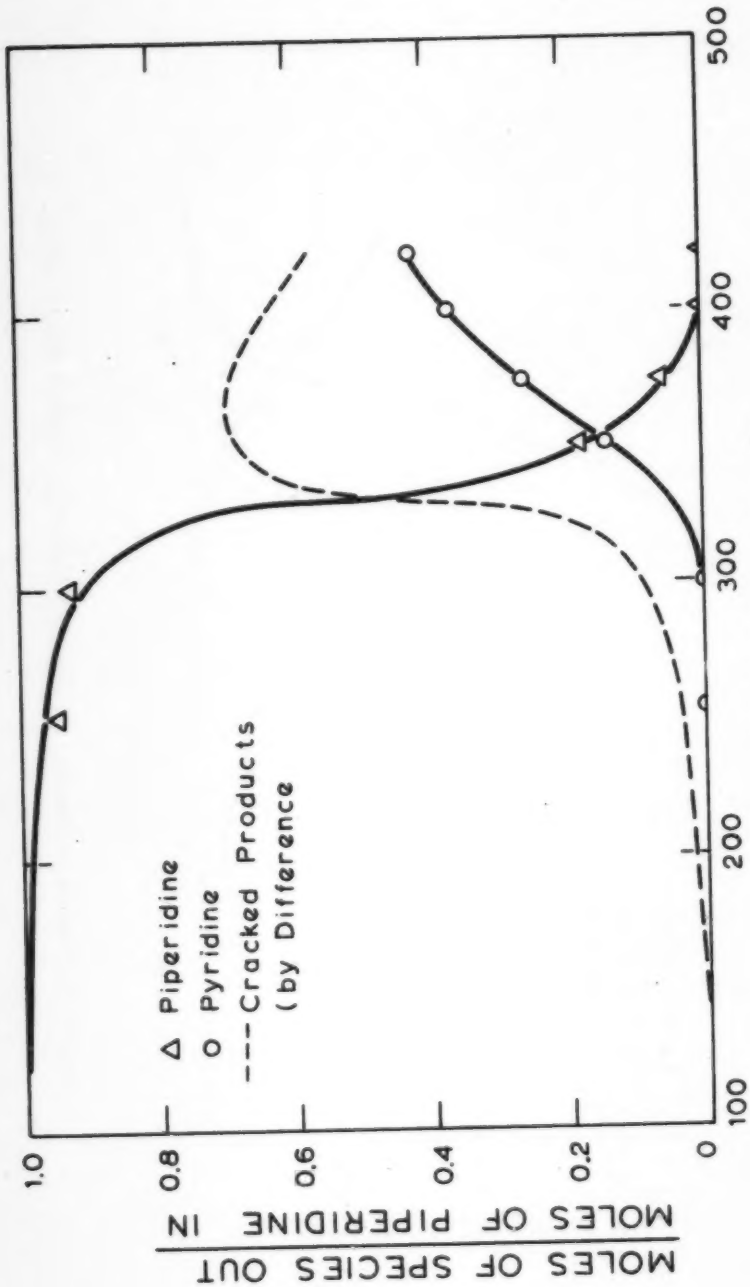


Figure 14. Product distribution for Piperidine HDN over NiMo/Al_2O_3 Catalyst.

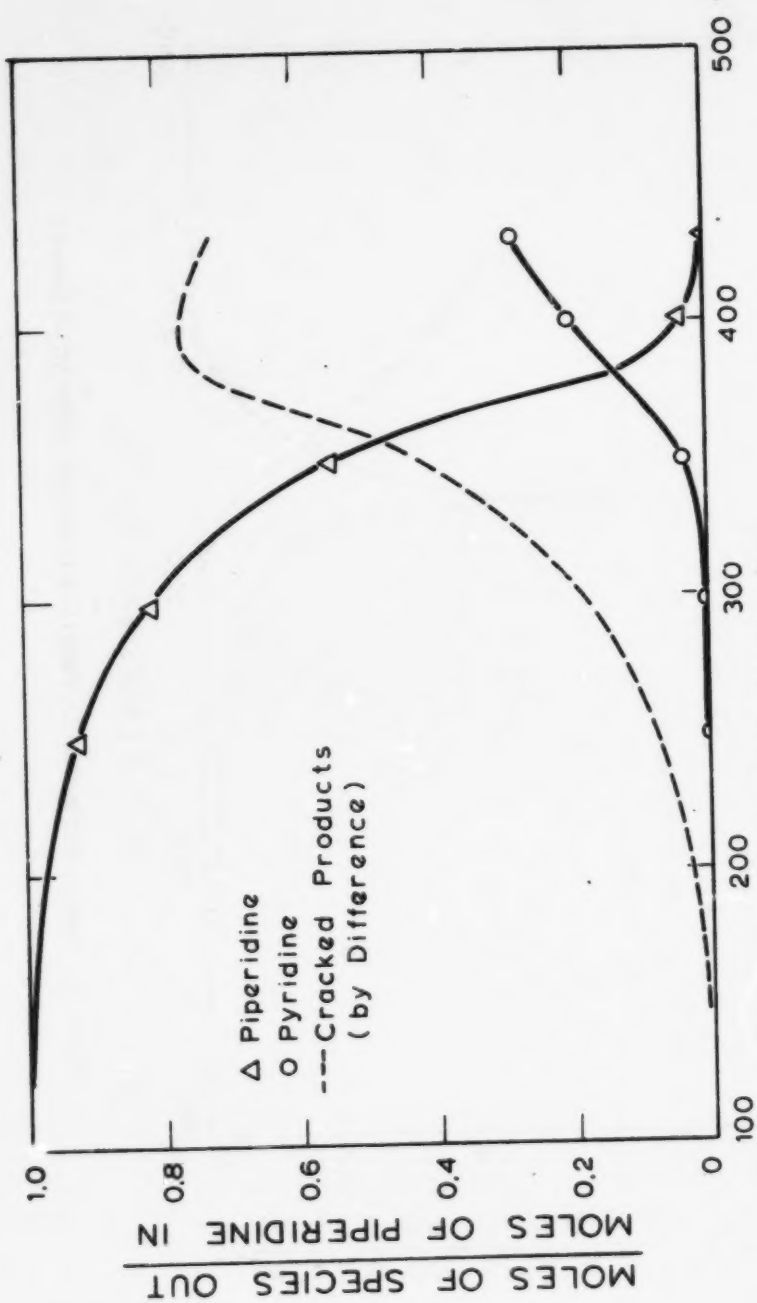


Figure 15. Product distribution for Piperidine HDN over CoMo/Al_2O_3 Catalyst.

idine dehydrogenation reaction was closer to equilibrium with $NiMo/Al_2O_3$ than with $CoMo/Al_2O_3$ (compare Figures 11 and 12).

6.3 Comparison with Previous Studies

Sonnemans et al. (1972) studied pyridine HDN over reduced $CoMo/Al_2O_3$ at 60 bars hydrogen partial pressure and Goudriaan (1974) at 80 bars pressure. No downturn in pyridine conversion was observed, though it appeared that the pyridine/piperidine equilibrium may have been established at 400°C. At the higher hydrogen pressures the equilibrium is much more favorable for piperidine than at the 11 bars hydrogen pressure used in the present study. The product distributions shown in Figures 9 and 13 exhibit the same trends as the distributions reported by Sonnemans and Goudriaan, except for the downturn.

McIlvried (1971) studied the hydrodenitrogenation of pyridine at 315°C and pressures of 50 to 100 bars on a $NiCoMo/Al_2O_3$ catalyst. He did not analyze for piperidine in his products but he observed that the nitrogen content of the total product was about the same for a given set of reaction conditions starting with either pyridine or piperidine. In his case the rate of hydrogenation of the pyridine ring was presumably rapid relative to subsequent steps and at his higher pressure there was no thermodynamic limitation on the concentration of piperidine that could exist in equilibrium with pyridine. Here the rates of hydrogenation of pyridine to piperidine and of the hydrogenolysis step both appeared to affect the overall rate at the lower temperatures. At the higher temperatures the rate-limiting step was solely hydrogenolysis of piperidine present in low concentration because of a thermodynamic limitation. The maximum in pyridine conversion at 375-400°C is caused by the decrease in the equilibrium concentration of piperidine with increased temperature being more important than the increase in the kinetic rate constant for piperidine cracking.

7. THERMODYNAMIC EQUILIBRIA OF SELECTED HETEROCYCLIC NITROGEN COMPOUNDS WITH THEIR HYDROGENATED DERIVATIVES

It was shown above that thermodynamics could cause a limitation on the rate of HDN of pyridine under some circumstances. The objective of this portion of the study was to extend these conclusions concerning the implications of thermodynamics to consideration of various steps involved in HDN of a group of representative heterocyclic nitrogen compounds found in natural and synthetic liquid fuels.

7.1 Heterocyclic Nitrogen Compounds in Petroleum

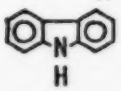
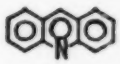
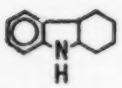
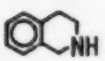
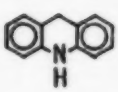
The heterocyclic nitrogen in petroleum and synthetic crudes is incorporated in five- or six-membered rings, most of which are unsaturated. Some representative compounds are shown in Table IV. These can be either basic or non-basic. Pyridines and saturated heterocyclic ring compounds (indoline, hexahydrocarbazole) are generally basic, while pyrroles tend to be non-basic.

The small quantities of non-heterocyclic nitrogen compounds present in liquid fules include anilines, aliphatic amines, and nitriles. These compounds are easier to denitrogenate by catalytic hydrogenation than the relatively unreactive heterocyclic compounds so they are not a serious problem.

Qader et al. (1968) reported that pyridines, quinolines, pyrroles, indoles, and carbazoles are the principal heterocyclic nitrogen structures present in low temperature coal tars. Indoles, pyridines, and their higher benzologs were reported in a California petroleum (Snyder, 1970). In this same study it was found that the nitrogen content increases with increasing boiling point (molecular weight) of the petroleum fractions. One- and two-ring heterocyclic compounds (pyridines, quinolines) predominate in the lighter fractions while the large multi-ring structures accumulate in the heavier fractions. Similar observations have resulted from studies of shale oils. Dinneen (1962) found that the nitrogen content of Colorado shale oil fractions increases continuously from about 1% (by weight) in

TABLE IV

Representative Heterocyclic Nitrogen Compounds

Name	Formula	Structure
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Isoquinoline	C_9H_7N	
Acridine	$C_{13}H_9N$	
Pyrrolidine	C_4H_9N	
Indoline	C_8H_9N	
Hexahydrocarbazole	$C_{12}H_{15}N$	
Piperidine	$C_5H_{11}N$	
1,2,3,4 - Tetrahydroquinoline	$C_9H_{11}N$	
1,2,3,4 - Tetrahydroisoquinoline	$C_9H_{11}N$	
9,10 - Dihydroacridine	$C_{13}H_{11}N$	

naphtha to over 2% in residuum. Pyridines and pyrroles account for most of the nitrogen in the naphtha fraction; pyridines, indoles, quinolines, tetrahydroquinolines, and more complex ring compounds are present in the heavier gas oil fraction.

The general conclusion from HDN kinetic studies that the multiring heterocyclic compounds are more difficult to denitrogenate than the lower molecular weight single- and double-ring compounds indicates that the higher boiling fractions which contain the most nitrogen also contain it in a form which is most difficult to remove.

7.2 Hydrodenitrogenation Mechanisms

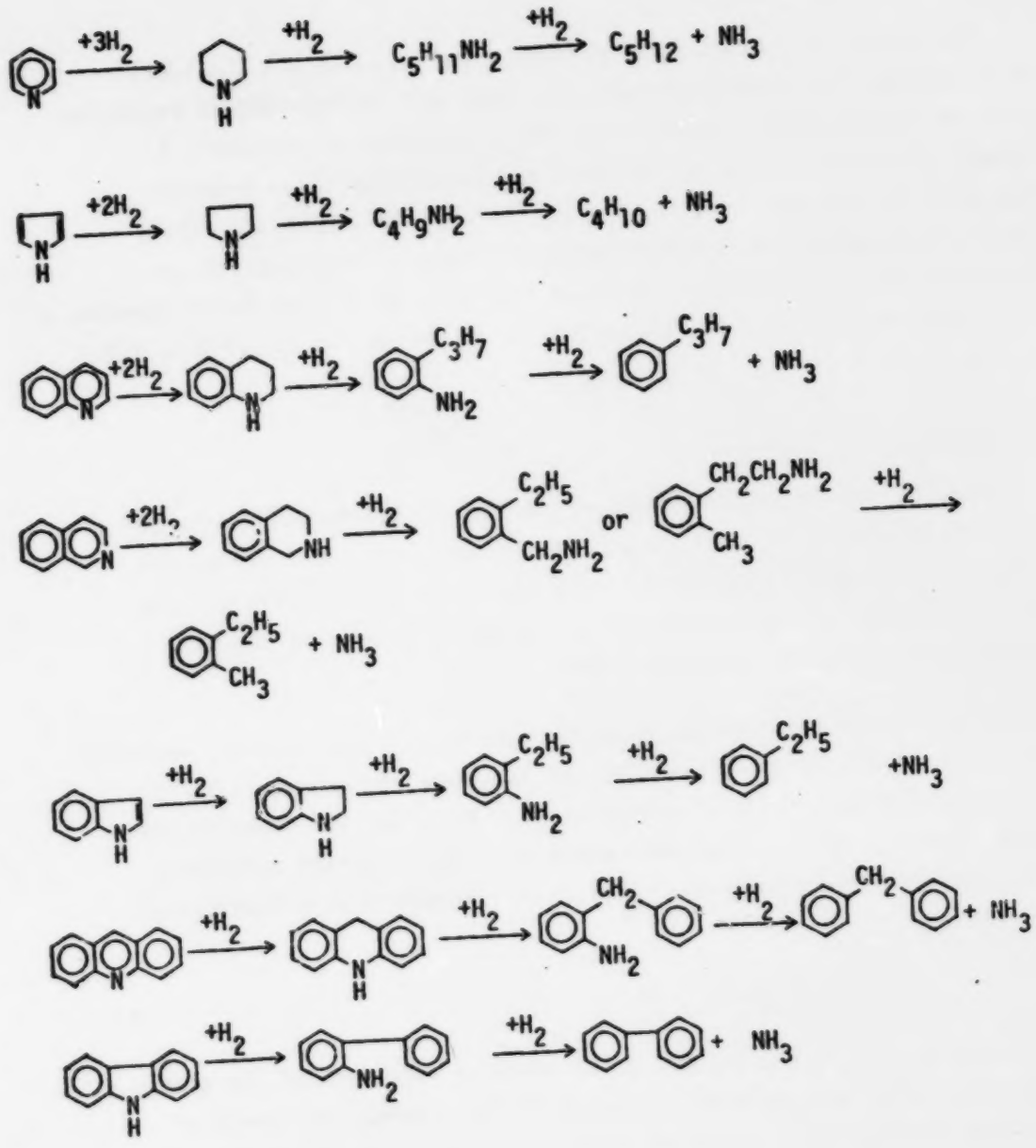
In present commercial practice hydrodenitrogenation proceeds incidentally to catalytic hydrodesulfurization at elevated temperatures and pressures. Most experimental work on HDN has been done at temperatures from 300 to 450°C (570-850°F) and pressures of 250-6000 psig.

In general hydrodenitrogenation of heterocyclic nitrogen compounds proceeds via saturation of the heterocyclic ring, followed by ring fracture at a carbon-nitrogen bond. Nitrogen is then removed from the resulting amine or aniline as ammonia. Ideally, HDN should selectively hydrogenate only the heterocyclic rings, avoiding saturation of desirable aromatics and olefins and minimizing hydrogen consumption.

Postulated HDN mechanisms of representative heterocyclic nitrogen compounds are shown in Table V. The mechanisms proposed for the following compounds are supported by experimental work: pyrrole (Smith, 1957), pyridine (McIlvried, 1971; Sonnemans et al., 1972, 1973, 1974), indole (Aboul-Gheit and Abdou, 1973; Hartung et al., 1961), quinoline (Aboul-Gheit and Abdou, 1973; Doelman and Vlugter, 1963; Madkour et al., 1969), and isoquinoline (Doelman and Vlugter, 1963; Madkour et al., 1969). Side reactions also occur. Sonnemans et al. (1972) reported disproportionation reactions in pyridine HDN and with two-ring compounds, aromatic ring saturation may occur, sometimes followed by ring fracture and scission of the saturated heterocyclic ring at a carbon-carbon or "aniline-type" carbon-nitrogen

TABLE V

Postulated HDN Mechanisms of Representative Heterocyclic Nitrogen Compounds



bond rather than at the weaker aliphatic carbon-nitrogen bond. Interconversion between quinoline and indole can even occur. The formation of β-cyclohexylethylamine, n-octylamine, N-ethylcyclohexylamine, β-phenylethylamine, and quinoline from indole HDN (Hartung et al., 1961) can be attributed to such side reactions.

The mechanisms proposed for carbazole and acridine are the ideal HDN mechanisms for these compounds, but they must be regarded as tentative. Horne and McAfee (1960) consider the denitrogenation of carbazole to biphenyl plausible, but also indicate that saturation of an aromatic ring prior to nitrogen removal is a possibility. Flinn et al. (1963) suggest that one of the carbazole aromatic rings is hydrogenated and cracked to form an alkylated indole or indoline, which then denitrogenates by the usual mechanism. No information on the mechanism of acridine HDN was found.

7.3 Calculation Procedures

Based on the proposed HDN mechanisms for the heterocyclic nitrogen compounds considered in this study, the thermodynamic equilibrium constants for the stepwise and overall HDN reactions were calculated from the corresponding standard free energy changes. Details of the calculations are given by Cocchetto (1974).

In most cases the free energies of formation of the relevant compounds were not available in the literature, so they were estimated, using the group contribution methods of Benson et al. (1969) and van Krevelen and Chermin (1951). The van Krevelen method resulted in direct estimation of the standard free energy of formation of a compound as a function of temperature:

$$\Delta G^\circ_f = A + BT \qquad (8)$$

The constants A and B are assumed to be additive functions of the atomic groups comprising the compound. Several of the original van Krevelen group contributions were rederived from more recent data to improve the accuracy of the estimations. Benson's method estimates the standard heat of formation and the corresponding standard entropy change. The standard

free energy of formation was then found as follows:

$$\Delta G^\circ_f = \Delta H^\circ_f - T\Delta S^\circ_f \qquad (9)$$

where ΔH°_f = standard heat of formation of a compound

ΔS°_f = standard entropy change for the formation of a compound from its elements.

Benson's method is generally more accurate than the method of van Krevelen, and is preferred for this reason. Unfortunately, Benson's method was not entirely applicable to all of the compounds encountered in this study, so some estimates had to be based primarily on van Krevelen's method. As much relevant thermodynamic data as could be found was compared with estimated values to determine the reliability of results. The ideal gas law was assumed and all species were taken to be in the gas phase.

7.4 Estimates of Reliability

7.4.1 Single-Ring Compounds: Standard heats and free energies of formation, at temperatures up to 1000°K, for pyridine, pyrrole, their hydrogenated derivatives, and ammonia are available in the literature. These data were used to calculate the thermodynamic equilibrium constants for the major steps in the pyridine and pyrrole HDN mechanisms and for the overall reactions. We estimate the absolute errors in the logarithms of the equilibrium constants for the hydrogenation steps to vary from about 0.4 at 298°K to 0.1 at 1000°K. The accurate free energies of formation for ammonia and the normal hydrocarbons do not introduce any significant errors in the results. The data for the aliphatic amines, however, are of questionable accuracy. Comparison of these data with the free energies of formation estimated from the methods of Benson et al. (1969) and van Krevelen and Chermin (1951) suggests that the literature values may be high by several kcal/mole. Thus the equilibrium constants calculated for the hydrogenolysis reactions (step 2) could be low by one or two orders of magnitude, while those for the denitrogenation reactions (step 3) could be high to the same degree.

7.4.2 Multi-ring Compounds: The calculations for the multi-ring heterocyclic compounds are based primarily upon estimated standard free energies

of formation since these data could not be found for most of the relevant compounds. Standard free energies of formation for ammonia and the hydrocarbon products, with the exception of diphenylmethane, were found in the literature and were used in preference to less reliable estimations.

The results are generally less reliable than those for the single-ring compounds. Errors in the estimated free energies of formation for diphenylmethane and the amine intermediates are less than 1 kcal/mole over the temperature range considered. These estimates are based on the relatively accurate Benson method which unfortunately is not completely applicable to the unsaturated and saturated heterocyclic nitrogen compounds. Free energy of formation estimates for these compounds, based on modified van Krevelen method, could be in error by several kcal/mole. As a result, calculated equilibrium constants for the hydrogenolysis reactions and the overall HDN reactions could be in error by one order of magnitude at 1000°K and two orders of magnitude at 500°K.

The equilibrium constants for the denitrogenation reactions (step 3) are more accurate since heterocyclic nitrogen compounds are not involved. The equilibrium constants for the ring-saturation reactions are less reliable because both unsaturated and saturated nitrogen heterocyclic compounds are present. The results for quinoline and isoquinoline are more reliable than the results for indole and the three-ring compounds, due to better estimates of the free energies of formation.

7.5 Results and Discussion

7.5.1 Single-Ring Compounds: Figures 16 and 17 present the common logarithms of the equilibrium constants for pyridine and pyrrole HDN respectively as a function of the reciprocal of the absolute temperature. The equilibrium constants in both figures always decrease with increasing temperature, consistent with the fact that all the reactions are exothermic. For both pyridine and pyrrole, the equilibrium constants for the initial ring-saturation steps are favorable ($K > 1$, $\log K > 0$) at low temperatures but become unfavorable ($K < 1$, $\log K < 0$) above approximately 225°C. The equilibrium constants for all the other reactions are favorable even at temperatures approaching 500°C.

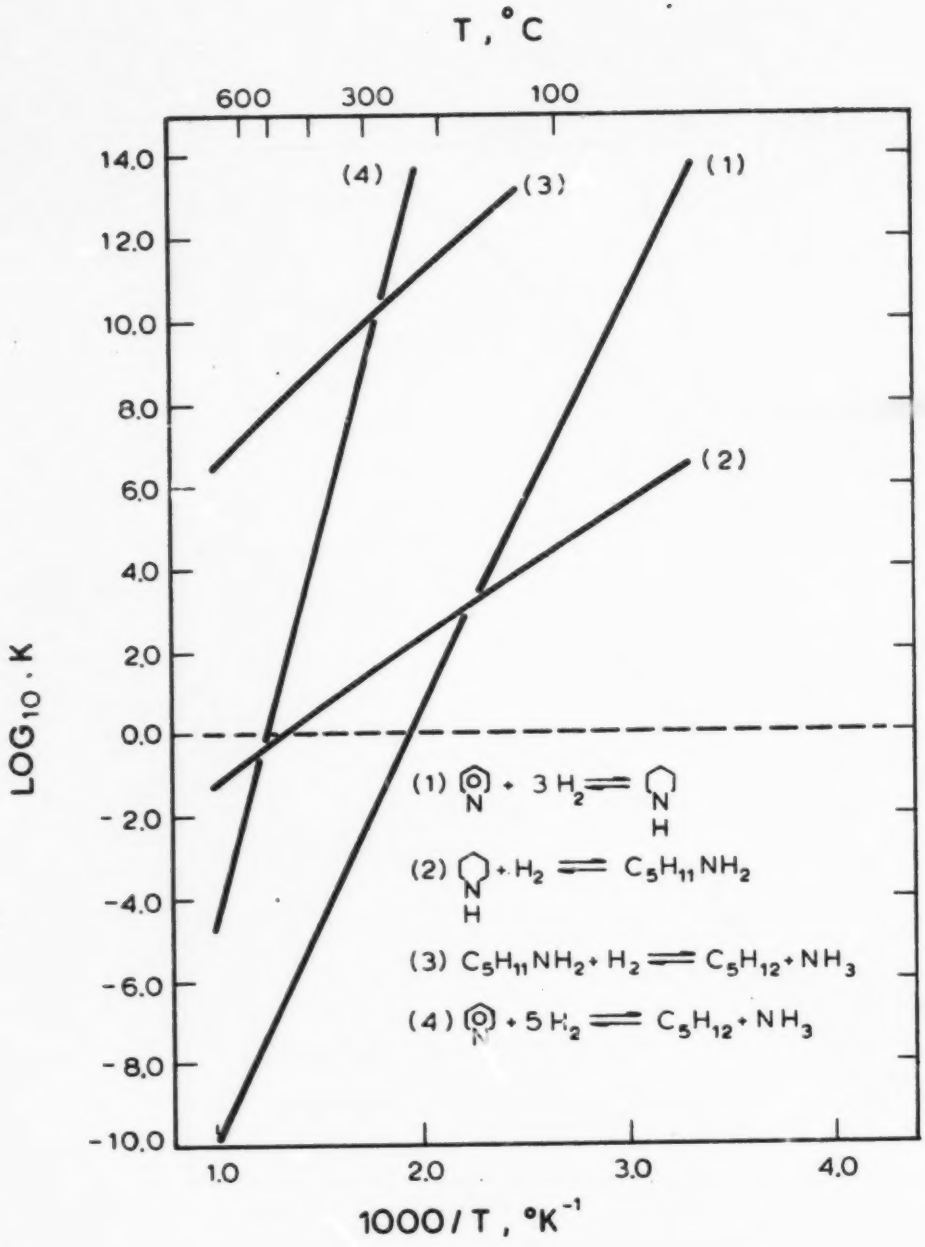


Figure 16. Thermodynamics of Pyridine HDN.

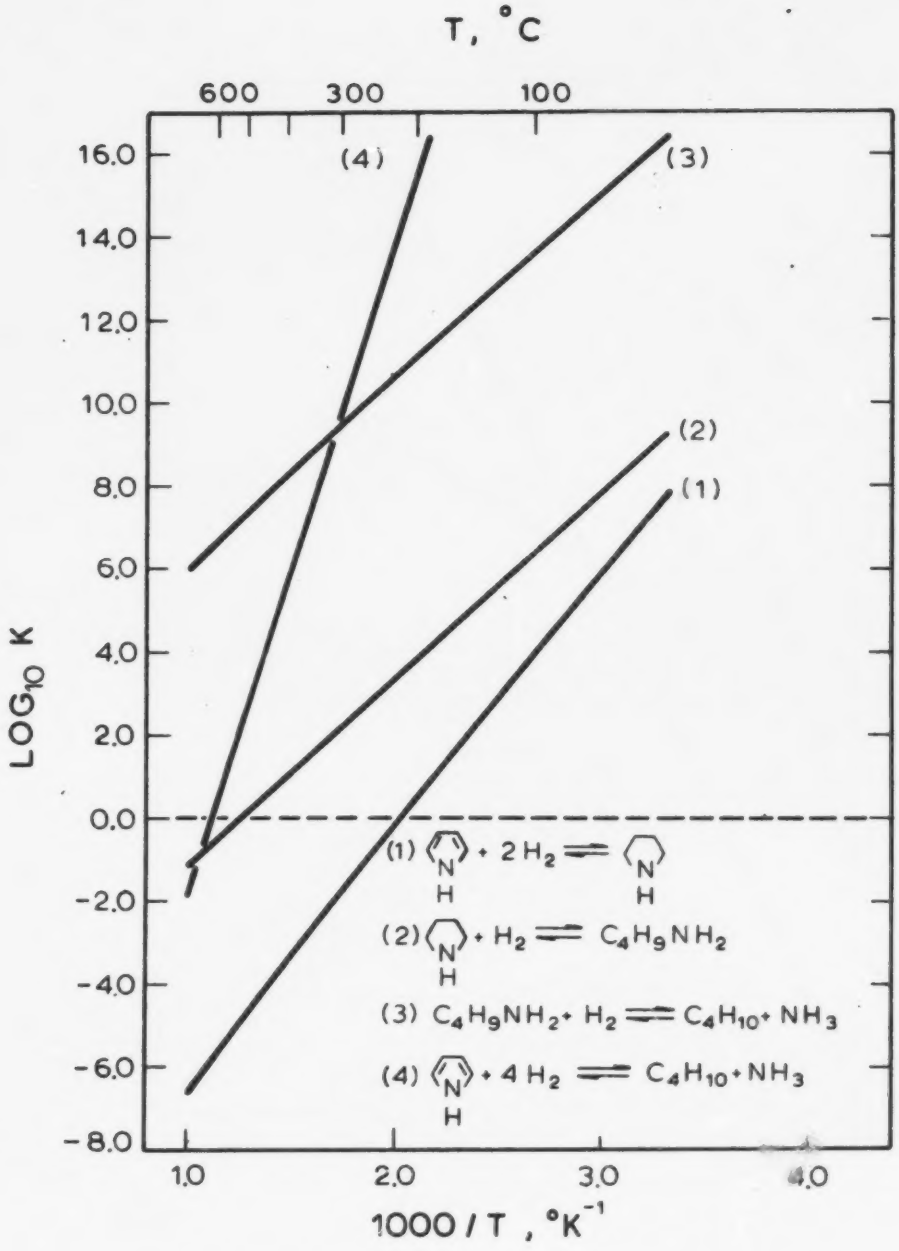


Figure 17. Thermodynamics of Pyrrole HDN.

There is generally a change in the total number of moles upon reaction, so pressure as well as temperature can affect the equilibria. Elevated pressure shifts the ring-saturation equilibria to the right (toward saturation) since the corresponding reactions are accompanied by a reduction in number of moles. Figure 18 shows, for example, the effect of temperature and pressure on the pyridine/piperidine equilibrium, which emphasizes the importance of hydrogen pressure.

7.5.2 Multi-Ring Compounds: Calculated thermodynamic equilibrium constants for the overall reactions and the steps in the HDN mechanisms of quinoline, isoquinoline, indole, acridine, and carbazole are presented in Figures 19 through 23. These are analogous to Figures 16 and 17 for the single-ring compounds. Qualitatively, the results for both the two- and the three-ring compounds are similar to the results for the single-ring compounds (note that the mechanism proposed for carbazole HDN does not include an initial ring-saturation step). The equilibrium constants for the ring saturation reactions are favorable only at low temperatures; those for the hydrogenolysis, denitrogenation, and overall reactions are favorable at temperatures as high as 500°C.

The relatively large uncertainties in some estimated equilibrium constants do not significantly affect these qualitative conclusions. The only exception is the equilibrium constant for the initial step in the proposed carbazole HDN mechanism (see Figure 23), for which there is considerable uncertainty. This reaction involves the hydrogenolysis of a resonance-stabilized pyrrole ring rather than a saturated or at least partially saturated heterocyclic ring, as in the other compounds considered. This initial step appears to be easier thermodynamically than ring saturation, but it is questionable whether the pyrrole ring in carbazole can be broken under HDN conditions prior to some degree of saturation. If the carbazole HDN mechanism involves some initial saturation of the aromatic rings, the equilibrium for this saturation step should be similar to the equilibria for the saturation steps in the HDN of the other heterocyclic compounds.

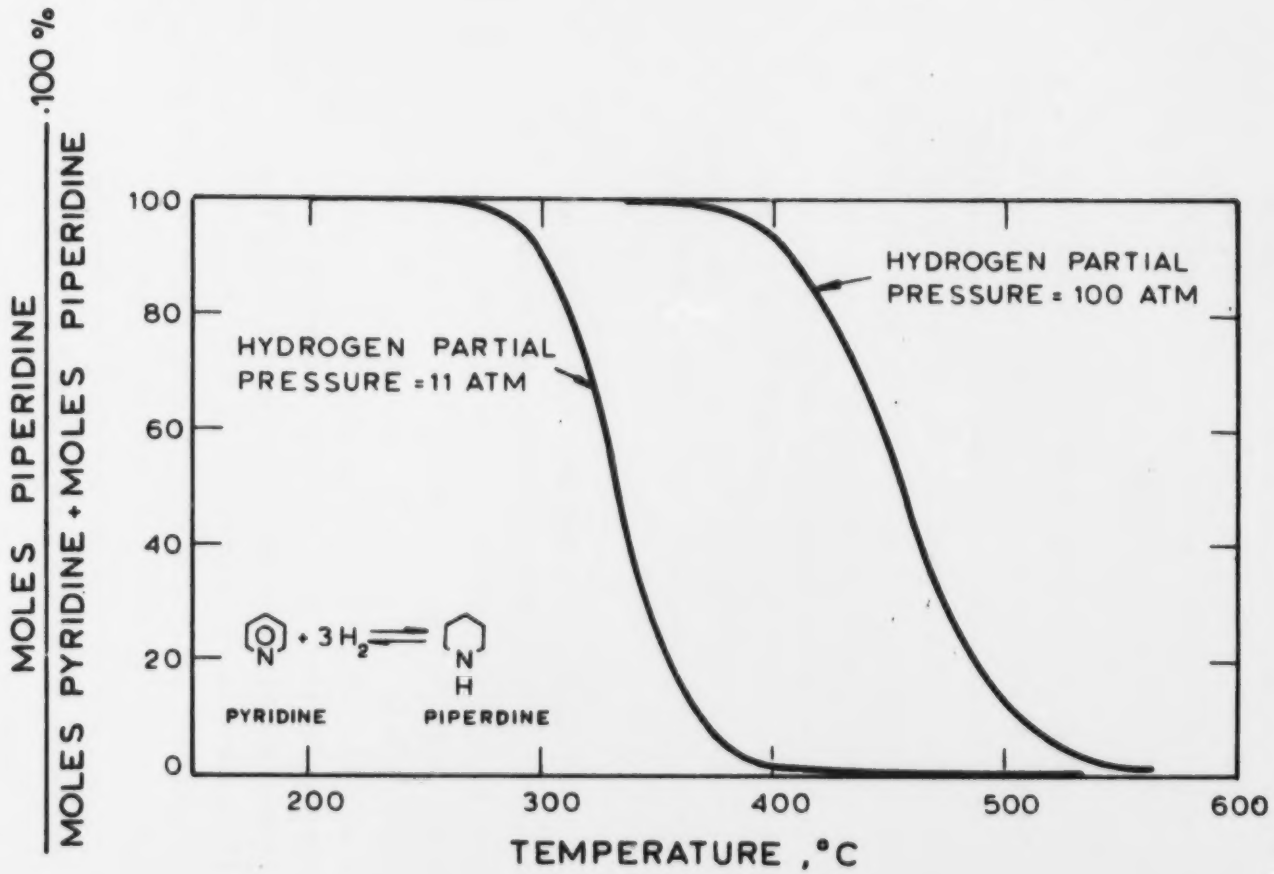


Figure 18. Calculated Pyridine/Piperidine Equilibrium.

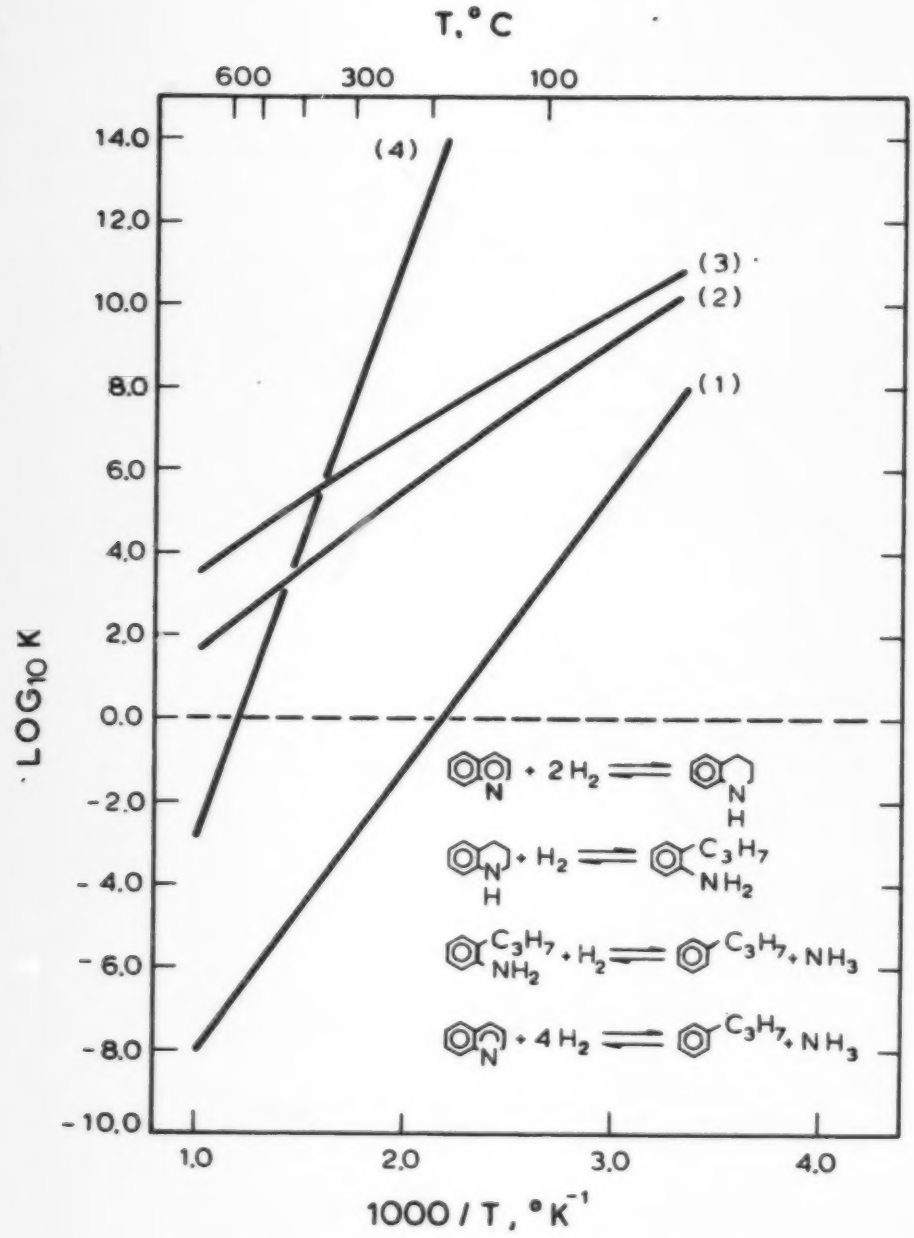


Figure 19. Thermodynamics of Quinoline HDN.

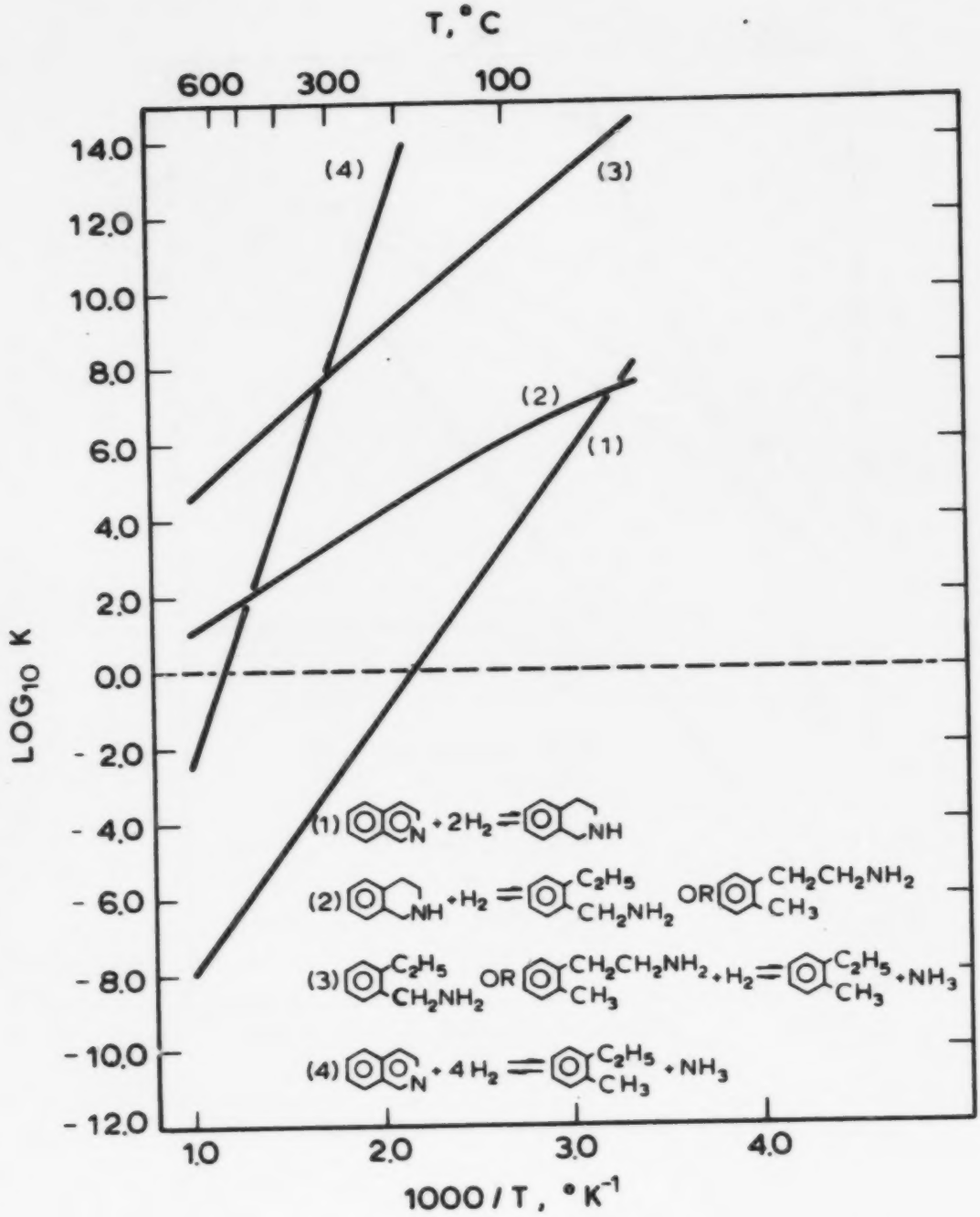


Figure 20. Thermodynamics of Isoquinoline.

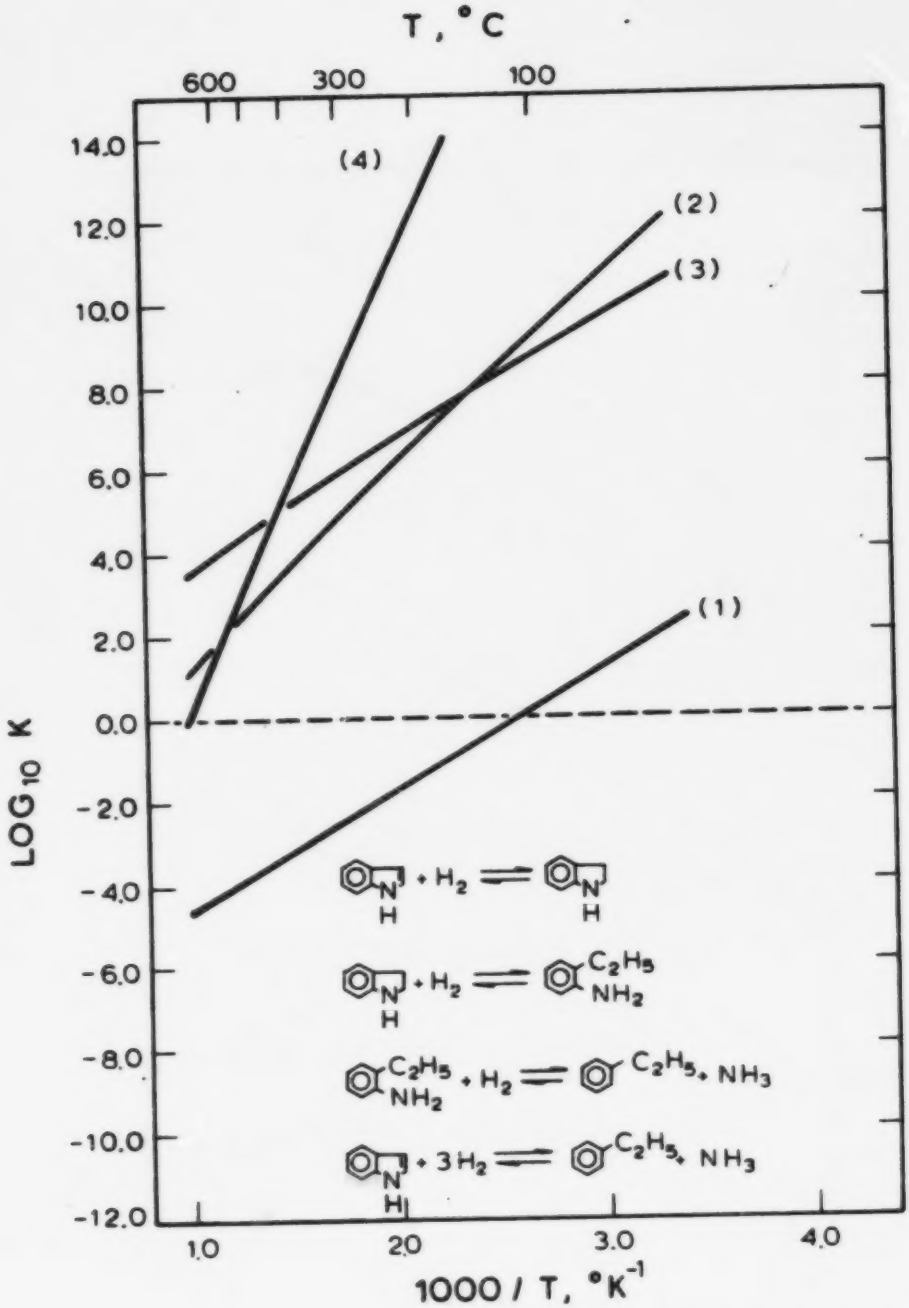


Figure 21. Thermodynamics of Indole HDN.

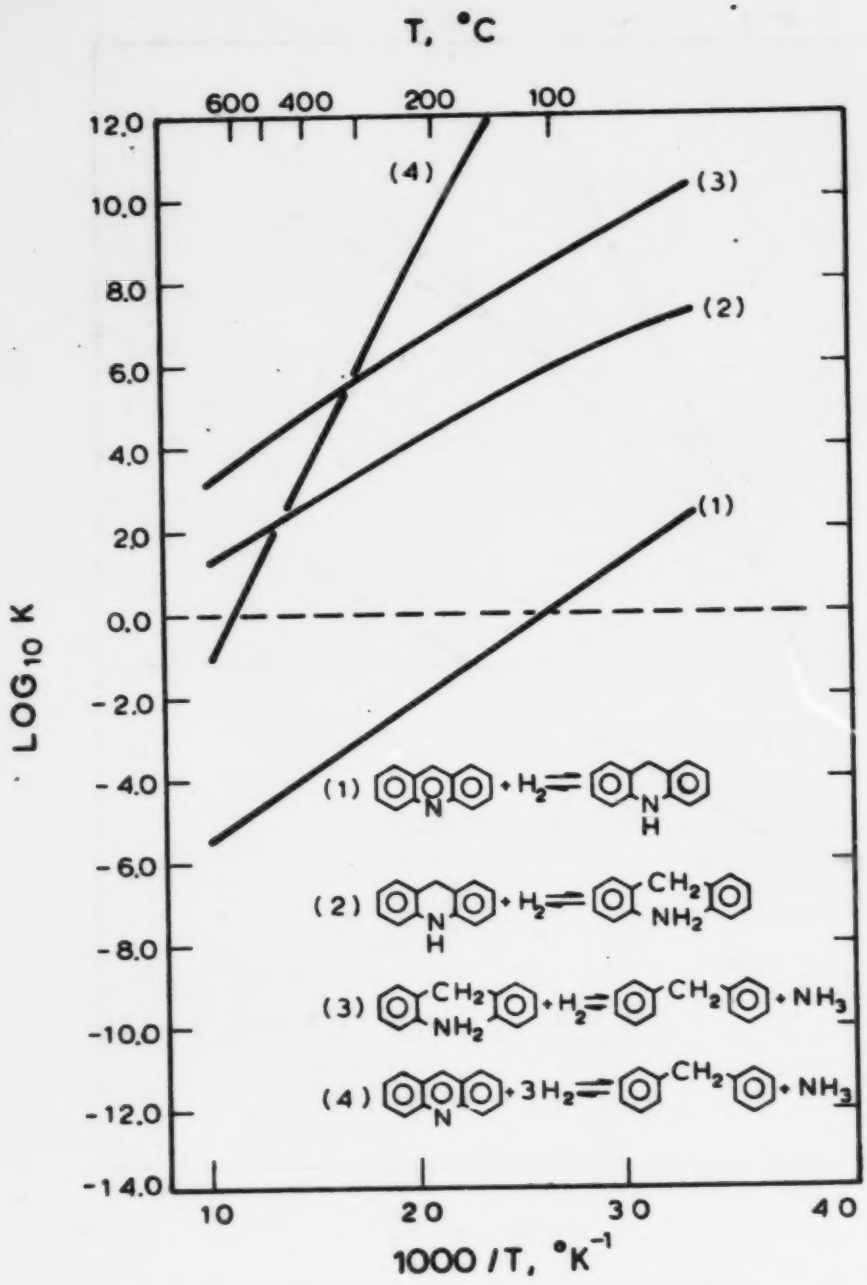


Figure 22. Thermodynamics of Acridine HLN.

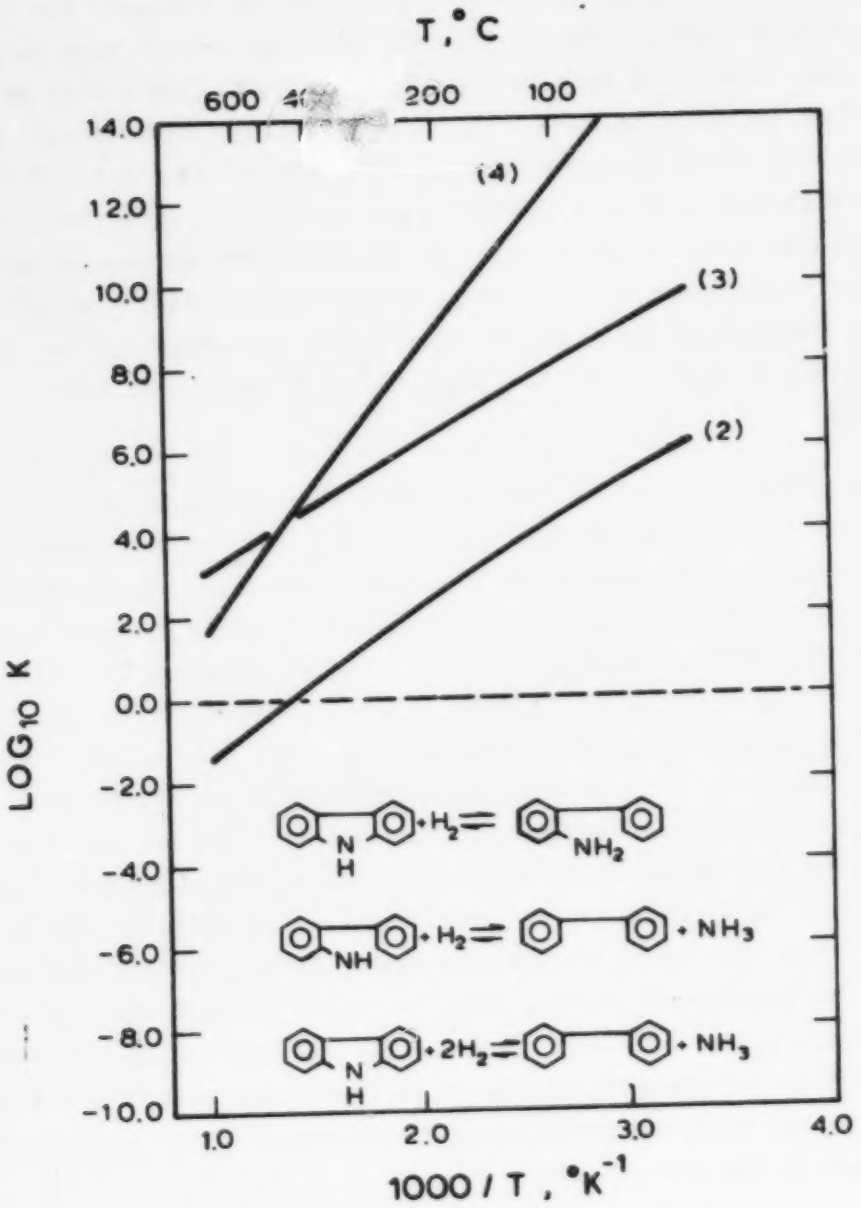


Figure 23. Thermodynamics of Carbazole HDN.

7.5.3 Effect of Operating Conditions: Increasing total pressure does not improve the denitrogenation equilibria, since there is no change in the number of moles upon reaction. The equilibrium constants for the hydrogenolysis steps and the overall HDN reactions are all very large at lower temperatures, but some decrease to about unity (log K = 0) as the temperature increases to 500°C. At this temperature only moderate pressure (10 atm) shifts these equilibria completely to the right. The initial heterocyclic ring-saturation step, however, is reversible; that is, appreciable quantities of both the saturated and the unsaturated heterocyclic compounds can be present at equilibrium within the relevant range of temperature and pressure. Decreasing the temperature or increasing the pressure shifts this equilibrium to the right, toward saturation.

The extent to which increased pressure can be used to overcome an unfavorable equilibrium constant depends, of course, on the number of moles of hydrogen consumed in the ring saturation step. Saturation of pyridine to piperidine requires three moles of H_2 while hydrogenation of indole to indoline requires only one. For an unfavorable equilibrium constant of say, 0.001 and a hydrogen partial pressure of 100 atm, the equilibrium piperidine/pyridine mole ratio is 1000, the indoline/indole ratio is only 0.1. Thus the elevated hydrogen pressure shifts the pyridine/piperidine equilibrium completely to the right but fails to make the indole/indoline equilibrium favorable for hydrogenation. Since the slope of log K versus 1/T is proportional to the enthalpy change on reaction, this also increases with the number of moles of hydrogen consumed in the hydrogenation step, which increases the exothermicity per mole of heterocyclic compound. Consequently the equilibrium concentration of the initial hydrogenated species is most sensitive to both pressure and temperature for those heterocyclic compounds consuming the greatest amount of hydrogen in the initial step.

7.6 Conclusions

The mechanism for the hydrodenitrogenation of heterocyclic nitrogen compounds involves reactions in series. Only the first step in this re-

action sequence is difficult thermodynamically. As a result, the effect of thermodynamics on overall HDN depends on the kinetics of the various steps in the mechanism.

If the initial heterocyclic ring-hydrogenation step is rate-limiting, the hydrogenated heterocyclic compound reacts as soon as it is formed and the position of the hydrogenation equilibrium for the initial step does not affect the overall HDN rate. If hydrogenolysis (cracking) (step 2) is rate-limiting, the reversible initial step can achieve equilibrium. The partial pressure of the saturated heterocyclic compound (the reactant for step 2) then depends on the position of the saturation equilibrium. The overall HDN rate in this case is the rate of hydrogenolysis, which in a simplified model depends on a temperature-dependent kinetic rate constant and on the partial pressure of the saturated heterocyclic compound, governed by the equilibrium of the first step. An increase in temperature increases the kinetic rate constant but decreases the equilibrium constant for the first step, decreasing the partial pressure of the reactant for the hydrogenolysis reaction. Thus the rate may go through a maximum with increased temperature. A potential thermodynamic limitation exists in most HDN mechanisms under those sets of circumstances in which hydrogenolysis of the C-N bond is slower than the rate of hydrogenation of the original heterocyclic ring and the equilibrium concentration of the hydrogenated compound is substantially limited.

8. NOTATION

k	intrinsic rate constant
K	adsorption coefficient
p	partial pressure
r	instantaneous reaction rate
H_2	hydrogen
P	pyridine
T	thiophene
I,II	type I, type II HDS sites

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